DETERMINATION OF ORGANIC SULFUR-CONTAINING STRUCTURES IN COAL BY FLASH PYROLYSIS EXPERIMENTS

William H. Calkins

Central Research and Development Department
Experimental Station
E. I. du Pont de Nemours & Company
Wilmington, Delaware 19898

Introduction

The sulfur in coal exists as both organic and inorganic forms. The inorganic forms are predominantly iron pyrite, although other metal sulfides and sulfates such as gypsum may also be present. ASTM tests [12,13] allow us to determine the total sulfur content of coals and the inorganic sulfur forms present. The total sulfur in organic structures is usually determined by difference, although electron microprobe can be used to determine it directly.

Despite its importance, there is only limited information in the literature on the chemical structures of sulfur in the organic components of coal. Attar [1,2,3,4,] has developed an interesting approach to determining the organic chemical structures of sulfur in coals by the programmed temperature reduction to H_2S. Discrete H_2S peaks are detected at various temperatures which presumably come from different sulfur entities. However, recovery of the sulfur has been low and interpretation of the results is difficult. LaCount [5] has developed a similar approach based on the programmed temperature oxidation to SO_2. SO_2 peaks are obtained at specific temperatures but assigment to particular sulfur structures is difficult and uncertain.

It was to see whether flash pyrolysis would provide an independent and new insight into coal sulfur structures that this research was undertaken.

Preliminary Experiments

Pyroprobe Pyrolysis

To identify pyrolysis products which might be expected from a more controlled pyrolysis of high sulfur coals, a Pyroprobe [6] programmed temperature solids pyrolyzer was connected to a GC/MS spectrometer (a Varian 3700 gas chromatograph with DB-5 column programmed from 60-230°C at 6°C min^{-1} coupled to a Micromass 16 mass spectrometer. Approximately 0.5 mg of coal was inserted into a 1 mm thin walled quartz tube and held in place with plugs of quartz wool. The tube was inserted in the pyroprobe and the temperature programmed from 250 to 1000°C at 20°C/millisec. The resulting mass patterns were resolved to identify the volatile sulfur compounds. Their yields were determined as area percent of total volatiles area. Results for one high sulfur coal - Pittsburgh 8-R&F - as the raw coal and as coal with most of the pyrite removed are shown in Table 1.

It can be seen by examination of Table 1 that a number of volatile or gaseous sulfur compounds are formed including H_2S, COS, CS_2, CH_3SH, and SO_2. In addition, many thiophenic compounds including thiophene, thianaphthene, and dibenzothiophene and most of the possible methyl derivatives of these three heterocyclic compounds are observed. No doubt many higher molecular weight heterocyclic compounds are formed which do not reach the mass spectrometer detector.

Removal of the mineral matter including the pyrite apparently reduces the SO_2, CS_2 and COS formed. With those exceptions, the products from the raw and low pyrite coals are qualitatively similar.

Solvent Extraction

To determine whether the sulfur species in coal are extractable or chemically bound into the coal structure, batch extraction experiments were carried out with four different solvents representing a range of solubility parameters (9.5-11.75). The extractions were run in 10 ml Hastalloy shaker tubes containing metal mesh baskets on the top sections to contain the coal. With solvent in the bottom section, the extractions were run at $100^{\circ}C$ for 4 hours with vertical shaking. The results are shown in Table 2.

As can be seen in the table, based on sulfur contents of the extracts, only a small fraction of the sulfur in the coal is solvent extractable.

Constant Temperature Flash Pyrolysis

A number of coals were pyrolyzed in the continous flash pyrolysis equipment shown in Figure 1. A Sigma 3B Perkin Elmer gas chromatograph equipped with a 3-column system and flame photometric sulfur detector provided sensitive analyses for the volatile sulfur products of coal pyrolysis.

The coal particles are entrained into the nitrogen stream in the feeder and carried over into the fluidized sand bed at the flash pyrolysis temperature. The coal pyrolyses in the sand bed and the volatile products are carried out of the reactor through a cellulosic thimble filter and much of the light char formed is entrained in the exit gas and carried into the filter also. Depending on the coal type, some of the coal is converted to coke in a process, going through a fluid or soft stage which remains on the sand particles or adhering to the reactor walls. Many of the high sulfur coals of particular interest in this study are so called "caking coals" which tends to make the sand particles adhere to each other. This creates problems in running the pyrolysis experiment by defluidizing the sand bed and plugging the inlet system to the reactor. While this often makes long pyrolysis runs difficult or impossible, in most cases, conditions can be used to provide adequate run life to get valid and useful data.

It is of interest to know how the sulfur in coal distributes itself among the various pyrolysis products. Not surprisingly, this depends upon the rank and sulfur components of the coal as well as the pyrolysis conditions. Table 3 shows the distribution of pyrolysis

451

products and sulfur containing products (as sulfur) of a typical high sulfur bituminous coal and a low sulfur lignite at 850°C. It will be noted that material recovery is good, despite the small amount of coal pyrolyzed. Sulfur recovery from the caking bituminous coal, however, is not as good. The pyrolysis products coat the reactor system and cannot be recovered for sulfur analysis. Also much of the coke remains on the sand and relatively large amounts of sand have to be analyzed for low levels of sulfur with some loss in accuracy.

Twenty-five to 50% of the sulfur in the coal (depending on the pyrolysis temperature) appears in the gaseous products as H_2S, CS_2, COS, and SO_2. The remainder of the sulfur appears in the tar, char, and coke, probably as stable thiophenic sulfur which remains in the coal structure or is released as heterocyclic compounds in the tar.

Preliminary Conclusions

One can surmise from these preliminary results that the organic sulfur in coal is largely chemically bound in the macromolecular structure of the coal, in part as labile, probably pendent, sulfur-containing side chains, and partly as heteroatoms in clusters of aromatic rings (thiophenic). Decomposition of the pendent groups probably accounts for much or all of the gaseous sulfur compounds (H_2S, COS, CS_2 and CH_3SH). The sulfur structures in the heterocyclic rings are stable at the temperatures used, but are partly broken away from the coal structures by rupture of other weaker carbon-carbon bonds: attaching these rings in the coal.

Continuous Flash Pyrolysis

Pyrolysis of Coal

To use pyrolysis to study the sulfur constituents of coal, it is necessary to know what sulfur containing products are produced and also what components in the coal are breaking down to produce them. The literature provides some clues as to the origins of some of these products:

When pyrite is pyrolyzed at temperatures of 550°C or higher, the initial breakdown[7] products are sulfur and pyrrhotite (FeS).

$$Fe\ S_2 \xrightarrow{\quad 550°C \quad} Fe\ S + S \qquad (1)$$
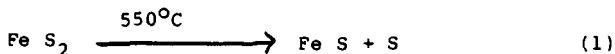
When the pyrite is in coal, the sulfur produced can react with hydrogen containing components of the coal (probably alkyl or hydroaromatic units) to form H_2S
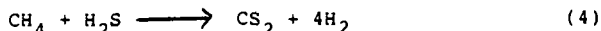
$$S + (Coal\ H) \longrightarrow H_2S + (Coal) \qquad (2)$$

Sulfur can also react with the coal matrix to form stable non-volatile products in the coal or coke[8,9].

At temperatures over 800°C, a significant amount of the H_2S or sulfur reacts with the coal to form carbon disulfide.

$$H_2S + (Coal) \longrightarrow CS_2 + H_2 \qquad (3)$$
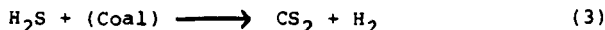
Similar reactions are observed when H_2S is reacted with methane,

$$CH_4 + H_2S \longrightarrow CS_2 + 4H_2 \qquad (4)$$

and since methane is produced in coal pyrolysis, this reaction may be a major route by which CS_2 is formed. The higher the pyrolysis temperature the larger the proportion of H_2S is converted to CS_2.

In most coal pyrolyses, a small amount of carbonyl sulfide is formed. Since COS is formed by reaction of CO and elemental sulfur, and substantial amounts of CO are formed on coal pyrolysis, it is likely that some sulfur formed by pyrite pyrolysis reacts with CO to form COS.

$$CO + S \longrightarrow COS \qquad (5)$$

It will be noted that when pyrite is low, the amount of COS produced is also small.

COS is also produced by pyrolysis of organic sulfoxides. However, these appear to be low or absent in most coals.

Some coals contain small amounts of sulfur as sulfates, although most of the sulfur in coal is in the reduced state. If these inorganic sulfates in coal are pyrolyzed in the presence of coal containing pyrite, SO_2 is formed. While the stoichiometry of this reaction has not been adequately demonstrated, it appears that the following reaction or something similar to it is going on.

$$CaSO_4 + FeS_2 + H_2O \longrightarrow CaO + FeS + 2SO_2 + H_2 \qquad (6)$$
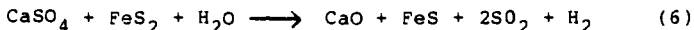
SO_2 is also formed in pyrolysis of organic sulfones. but these appear to be very low or absent in most coals.

Pyroprobe pyrolysis of coal shows formation of small amounts of methyl mercaptan, and model compounds containing $-SCH_3$ groups pyrolyzed at low temperatures ($600^\circ C$ and lower) do form methyl mercaptan. However, little of this compound is observed in our continuous coal pyrolysis experiments.

Pyrolysis of Model Sulfur Compounds

To learn the behavior of the various types of organic sulfur structures in pyrolysis, a series of solutions of low molecular weight sulfur compounds was prepared in benzene at concentrations roughly approximating the organic sulfur content in high sulfur coals. Using a precise piston pump and vaporizer, these compounds were introduced into the pyrolyzer at rates roughly comparable to the rates used in pyrolyzing coal. Pyrolysis temperatures of 600, 700, 800, 850, 900 and $950^\circ C$ were used. Some 16 model sulfur compounds were pyrolyzed at the various temperatures. Figure 2 shows conversion of some of these compounds at various temperatures. This shows that aliphatic and benzylic sulfides, mercaptans and disulfides split out H_2S at relatively low temperatures ($600-800^\circ C$). Aromatic sulfides and mercaptans require $900^\circ C$ to give high conversions to H_2S and CS_2. The three major thiophenic compounds, thiophene, thianaphthene, and dibenzo-thiophene show only a relatively low conversion even at $950^\circ C$. This provides a basis for differentiating between sulfur types in coal.

However, this assumes that the sulfur compounds in coal behave similarly to the model compounds investigated. There is no obvious way to show whether this is true or not. It was reasoned, however, that a polymeric sulfide would more nearly approximate the organic sulfur containing structures in coal. To test this, approximately 5% of Aldrich polyphenylene sulfide (10,000 mol wt) was added to anthracite and epoxy resin, cured, ground, sieved and fed to the pyrolyzer at 900, 910 and 920°C. Yields of pyrolysis products from this sample suggests that polymeric aromatic sulfides are perhaps slightly more stable than the corresponding monomeric sulfur compounds although not greatly different.

In continously pyrolyzing coal or model sulfur compounds it is important to establish a steady state condition with respect to all the pyrolysis products before meaningful results can be obtained. There appears to be a great difference between the various pyrolysis products in the rate at which this steady state is achieved. COS and CS_2 tend to level out quite rapidly after a steady coal feed rate is achieved; H_2S, on the other hand, is quite slow. This is probably due to chemi or physisorption on the walls of the system. Since H_2S is the largest single sulfur product of coal pyrolysis, it is extremely important that sufficient time be allowed to attain a steady state.

## Pyrolysis of a Typical High Sulfur Bituminous Coal

A raw Pittsburgh 8 R&F coal was pyrolyzed at 600, 775, 850, 900, 925, 950, 975 and 1000°C. The principal product was H_2S at all temperatures but over 850°C, CS_2 is formed at the expense of H_2S. Small amounts of COS were also formed at all temperatures. Unlike the pyrolysis in the pyroprobe and the pyrolysis of such model compounds as thiocresol at 600°C, no methylmercaptan was observed even at 600°C.

Figure 3 shows a plot of combined sulfur yield as COS, H2S, and CS_2 vs. pyrolysis temperature. It also shows individual yields of H_2S, and CS_2 vs. pyrolysis temperature. It is to be noted that sulfur yield appears to level off at 775 to 900°C and then drops precipitously. Also, H_2S is by far the major product up to 800°C but above that, the H_2S starts to drop as CS_2 is formed.

The drop above 900°C in the amount of total sulfur volatilized raises a number of questions concerning what is occuring. It does not appear to occur in the pyrolysis of the low molecular weight model compounds. To make sure the drop when coal is pyrolyzed was not associated with H_2S absorption of basic components in the coal mineral matter, the same coal was boiled with dilute HCl, washed with distilled water and dried. Pyrolysis of that coal at 1000°C gave roughly equivalent results as the untreated raw coal.

There is evidence in the literature that H_2S or sulfur can react with coal or coal char at high temperatures [4,8,9]. Energetically, for this reaction to occur at such high temperatures, the product must be very thermally stable. It also raises the question whether this reaction consuming H_2S is affecting our results at 900°C. Table 4 shows the rate constants (assuming first order kinetics) for the high temperature reaction at various temperatures and Figure 4 is an Arrhenius plot of these data. The activation energy of 56 kcal suggests that chemical bonds are being made or broken. The data also indicates that the H_2S consuming reaction is

very slow indeed at 900°C and not likely to interfere significantly with the 900°C pyrolysis measurements. Attar[4] has observed this H_2S absorption phenomenon and explains it as reaction of the H_2S with coke or char to form thiophenic structures.
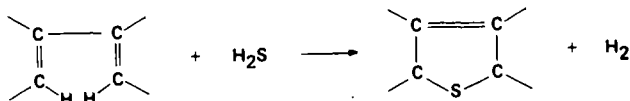
        This is consistent with the known high stability of the thiophenic structures and the fairly high activation energy we observe.

Pyrite

        While pyrolysis appears to be a promising approach to determining the composition of the organic sulfur components in coal, the presence of iron pyrite in such large amounts as are present in high sulfur coals, presents a serious problem as mentioned previously. Pyrite, like organic sulfur compounds, when pyrolyzed in the presence of coal also produces H_2S at temperatures around the decomposition temperature of pyrite (around 550°C) and H_2S and CS_2 at higher temperatures (over 850-900°C) An effort was therefore made to remove the pyrite and other inorganic sulfur from the coal ground to 1μ size, before the pyrolysis studies were carried out. However, even with combinations of both sink/float and the Otisca solvent agglomeration processes, about 10% of the original pyrite remained in the coal as indicated by iron analysis (atomic absorption). The reason for the difficulty in pyrite removal became apparent when STEM Scanning Transmission Electron micrographs were made of the fine particles after pyrite "removal". They showed pyrite particles in the range of 0.1 to 0.6μ size inside the coal particles. These could not be removed from the coal unless it was ground much finer than 1μ.

        It was decided, therefore, for pyrolysis studies to prepare each coal with several known different pyrite concentrations by partial pyrite removal. The pyrolysis results would then be extrapolated to zero pyrite concentration.

        A series of five (5) samples of Pittsburgh 8 R&F coal containing various levels of pyrite was pyrolyzed in the pyrolyzer (Figure 1). The sum of the yields of COS, H_2S, and CS_2 at 600, 775, 850 and 900°C are plotted against actual pyrite concentration in Figure 5. There is a fair amount of scatter in the data. This scatter is due in part to variations in gas rate and coal feed rate and in determining the pyrite concentration. However, a set of reasonably straight lines is defined which can be extrapolated to 0 pyrite concentration. Some conclusions can be drawn from these data. 1) There is little or no difference in the data obtained at 775°C and that obtained at 850°C, suggesting that all the aliphatic sulfur compounds are broken down by 775°C and either the aromatic sulfur species are low in concentration or have not yet started to break down at 850°C. 2) There is only a relatively small difference between the 900°C line and the 775°C and 850°C line, supporting the idea that the aromatic sulfur compounds are very low in concentration. 3) The slope of the 600°C line is about 0.21 gram sulfur/gram of pyritic

sulfur which is considerably under the theoretical value of 0.5 for the breakdown of pyrite to pyrrhotite. 4) In the 775-900°C temperature range, the slope increases to around 0.27-0.30. Apparently about 54 to 60% of the sulfur liberated in the pyrite pyrolysis reacts with the coal matrix at those temperatures to form H_2S. The rest forms COS or is trapped in the coal or coke structure. 5) The intercept of this 775-850°C line occurs at 0.82% sulfur which represents approximately 40% of the total organic sulfur in the coal as aliphatic sulfur. The 900°C intercept occurs at about 0.83% sulfur representing an additional approximately 1% as aromatic sulfur. Presumably, the remaining 59% of organic sulfur is thiophenic or stable sulfur compounds of some kind.

Another problem associated with the mineral matter of the coal was due to the basicity of some mineral matter. If the mineral matter of the coal contains a significant amount of basic material, it may absorb some of the sulfur containing acid gases (H_2S, SO_2) produced in pyrolysis and thereby prevent them from entering the analytical system. Acid treating of the coal, however, resulted in only slight increase in the H_2S produced on pyrolysis of the bituminous coals tested. The acid washed lignite gave approximately 20% higher sulfur volatile yield, however, than the untreated.

Pyrolysis of 3 Additional High Sulfur Coals

Three additional high sulfur coals were prepared at two or three pyrite concentrations each. These were pyrolyzed at two temperatures - 775°C and 900°C. They represent temperatures at which most of the aliphatic and most of the aromatic sulfur compounds should be broken down, respectively. Little or none of the thiophenic compounds should be affected at those temperatures.

The results of these pyrolyses are plotted in Figure 6. It will be noted that as was the case with Pittsburgh 8 R&F, the 775°C and 900°C lines are very close together indicating very little (only 1-4%) aromatic sulfur compounds present. However, in each case, a substantial portion (30-40%) of the organic sulfur is aliphatic sulfur. The rest is assumed to be thiophenic.

The slopes of the 900°C lines were approximately 0.27 gms of sulfur/gram of pyritic sulfur suggesting that this slope can be used in future determinations with other coals.

## Organic Structures Containing Sulfur in Coals of Various Ranks

Distribution of Sulfur Types

Four additional coals of various ranks were pyrolyzed and the zero pyrite point estimated using the slope of .27. An estimate of the distribution of organic sulfur types in 8 different coals is shown in Table 5. This of course assumes that all sulfur compounds obtained on pyrolysis at 775-850°C or lower is aliphatic mercaptan or sulfide, and that sulfur compounds obtained from 850-900°C are aromatic mercaptans or sulfides. Organic sulfur structures not pyrolyzing at 900°C or lower are assumed to be primarily thiophenic. These assumptions are challengeable as mentioned previously on the basis that sulfur in a macromolecular structure such as coal may behave

differently than model compounds on pyrolysis and that substituents of various types in coal may activate or deactivate the sulfur structures so that they pyrolyze somewhat differently. Nevertheless, these results do suggest that the organic sulfur in coal is mainly aliphatic and thiophenic. Low rank coals appear to have higher proportions of aliphatic sulfur and as rank increases, the thiophenic proportions increase.

Thioethers or Mercaptans?

This pyrolysis method does not distinguish between mercaptans and thioethers. In an effort to determine whether the sulfur is mercaptan, thioether, or both, an independent analytical method was resorted to. This method, first tried by Russian workers, depends on the reaction of methyliodide with mercaptans and thioethers[10,11].

$$RSR' + CH_3I \quad ------ \quad RSR'I^{-}_{+} \qquad (8)$$

$$RSH + CH_3I \quad ------ \quad RSCH_3 + HI \qquad (9)$$
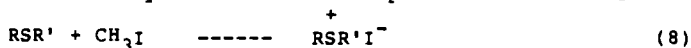
If there is mercaptan present, some titratable acid should be formed. If there is thioether present, iodide should remain in the coal and could be determined quantitatively. The results of this test on three high sulfur coals are shown in Table 6. While this reaction does not appear to be highly reproducible or quantitative, it does indicate that a significant amount of the organic sulfur in coal is present as thioether and there is little if any sulfur present as free mercaptan.

These experiments together with the pyrolysis runs, suggests that the sulfur in coal is present as aliphatic thioether side chains and as heteroatoms in the aromatic ring clusters.

Estimate of Pyrolysis Rates

The degradation rates of the model compounds studied were obviously quite high since almost complete conversion of the aliphatic sulfur compounds was obtained at $775^{\circ}C$ and of the aromatic sulfur compounds at $900^{\circ}C$ and the nominal hold-up time of about 0.5 seconds. With high sulfur coals, however, the coal melts and much of it remains as coke on the sand particles. Do the sulfur groups in the coal pyrolyze as fast as the model compounds did or do they break down more slowly? This would provide a clue as to whether the sulfur compounds in coal do behave like their low molecular weight models.

To try to answer this question, Pittsburgh 8 R&F coal was pyrolyzed at $900^{\circ}C$ and $775^{\circ}C$ by feeding the coal to the pyrolyzer at those temperatures until a steady state rate of H_2S, CS_2 and COS evolution was observed as had been seen previously. The coal input was then stopped suddenly and the evolution of H_2S, CS_2 and COS evolved determined at one minute intervals. In both experiments, the evolution of these compounds dropped abruptly with little or nothing observed even at the first minute.

A similar test run at 700°C when the aliphatic sulfur breakdown should be slower, showed roughly a third of the steady state H_2S coming off after one minute and small amounts of CS_2 and COS. The sample taken at two minutes show none of these compounds.

These results support the view that the labile sulfur compounds in coal break down at rates similar to those of the model compounds.

Acknowledgement

References

1. Attar, A., "Sulfur Groups in Coal and Their Determination", Chapter 56, Analytical Methods for Coal and Coal Products, Vol III Karr-Academic Press
2. Attar, A; Corcoran, A. H.; and Gibson, G. S., ACS Fuel Division Preprints 21 (7) 106 (1976)
3. Attar, A. and Dupuis, F., ACS Fuel Division Preprints 23 (2) 44-53 (1978)
4. Attar, A., DOE Report DOE/PC/30145-Tl (DE 84007770)
5. LaCount, R. B., et al, New Approaches in Coal Chemistry, ACS Symposium Series 169 pps 415-426
6. Chemical Data Systems (CDS), Oxford, Pa.
7. Luganov, V. A. and Schebalin, V. I., Can. Met. Quart. 1982, 21, 157
8. Stewart, I., et al, ACS Fuel Division Preprints 29 (4) 341 (1984)
9. Boehm, H.P.; Hofmann, V. and Clauss, A., Proc. 3rd Conf. on Carbon, Pergamon Press, N.Y. p241 (1957)
10. Postovski, J. T. and Harlamgovish, A. B., Fuel 1936 15 229-232
    11. Bogdanova, V. A. and Boranski, A. D., Kratk Soobshch. Nauchno-Issled Rabt. 2a, Sb68 (cs 63 1774 b (1965)
12. ASTM D3177-75 "Total Sulfur in the Analysis Sample of Coal and Coke"
13. ASTM D2492-68 "Forms of Sulfur in Coal"

Table 1

PYROPROBE GC/MS ANALYSIS OF
PITTSBURGH 8-R & F HIGH SULFUR COAL

(% of Total Area)

	Raw	90% of Pyrite Removed
H_2S	3.03	4.83
COS	0.48	0.31
CH_3SH	0.32	0.34
SO_2	2.13	0.02
CS_2	0.27	0.06
Thiophene	0.25	0.22
Methylthiophene-1	0.34	0.23
Methylthiophene-2	0.23	0.10
Dimethylthiophene-1	0.49	0.46
Dimethylthiophene-2	0.47	0.38
Dimethylthiophene-3	0.38	0.24
Dimethylthiophene-4	0.07	0.05
Trimethylthiophene-1	0.19	0.10
Trimethylthiophene-2	0.22	0.16
Tetramethylthiophene	low	0.04
Benzothiophene	0.29	0.24
Methylbenzothiophene-1	0.06	0.04
Methylbenzothiophene-2	0.13	0.15
Methylbenzothiophene-3	0.20	0.19
Methylbenzothiophene-4	0.15	0.14
Methylbenzothiophene-5	0.17	0.12
Methylbenzothiophene-6	?	0.02
Dimethylbenzothiophene-1	0.11	0.11
Dimethylbenzothiophene-2	0.06	0.05
Dimethylbenzothiophene-3	0.12	0.14
Dimethylbenzothiophene-4	0.07	0.10
Dimethylbenzothiophene-5	0.05	0.04
Dimethylbenzothiophene-6	0.07	0.08
Dimethylbenzothiophene-7	0.05	0.04
Dimethylbenzothiophene-8	0.05	0.03
Dimethylbenzothiophene-9	0.03	0.02
Dibenzothiophene	0.08	+

*Number does not denote chemical structure but an
arbitrarily assigned isomer number.

Table 2

SOLVENT EXTRACTION OF COALS

Pittsburgh 8—R & F 200 mesh (4.65% S)
100°C/4 hrs w/shaking

	%S in Extract	% of S Extracted
Acetonitrile	0.10	4.7
Pyridine	0.09	4.3
Tetrahydrofuran	0.33	14.2
Ethylenediamine	0.07	3.3

Table 3

COAL PYROLYSIS PRODUCTS
MATERIAL AND SULFUR BALANCES

	850°C			
	Pittsburgh 8 R & F		Alcoa Texas Lignite	
	Wt %	% of the Sulfur	Wt %	% of the Sulfur
Gas	21.8	49.5	36.3	48.4
Tar	11.9	7.3	5.5	8.8
Char	6.4	1.7	31.1	31.4
On Sand & Reactor	43.0	24.5	29.1	1.3
Trap Head	6.5	?	.01	
TOTAL	89.6	81.1	101.7	90.0

Table 4

RATE CONSTANTS FOR
HIGH TEMPERATURE ABSORPTION OF H_2S
(Assumes First Order Kinetics)

Temperature °C	Rate Constant (Sec^{-1})
900	ca 0
925	.167
950	.497
975	.801
1000	1.233

Table 5

ORGANIC SULFUR SPECIES IN COALS STUDIED

	Total Sulfur wt %	Organic Sulfur wt %	% of Organic Sulfur			BTU
			Aliphatic Sulfides & Mercaptans	Aromatic Sulfides & Mercaptans	More Internally Stable Types (Thiophenic) (By Diff.)	
Alcoa Texas Lignite (Wilcox)	1.30	.73	82	<1	18	10,555
Emery (Utah)	1.19	0.57	61	1-2	39	12,710
Pittsburgh 8-Shoemaker	4.00	1.36	53	<1	46	12,991
Pittsburgh 8-R & F	4.85	1.63	49	1-2	49	12,156
Pittsburgh 8-McElroy	5.47	1.58	49	<2	49	13,098
Ohio 9-Egypt Valley	2.49	1.46	44	<1	55	13,175
Illinois 6-Burning Star	3.24	2.04	39	2	59	12,165
Anthracite - Lehigh Valley	0.90	0.6	0	0	100	14,245

Table 6

THIOETHER AND MERCAPTAN GROUPS
IN HIGH SULFUR COALS

(By Reaction with CH_3I)

	% Organic Sulfur	% of Organic Sulfur	
		As RSR′	As RSH
Pittsburgh 8-R & F	1.63	33.0	4.3
Pittsburgh 8-Shoemaker	1.40	30.4	2.5
Illinois 6-Burning Star	2.04	22.4	4.9

Figure 1

Fluidized Bed Pyrolyzer
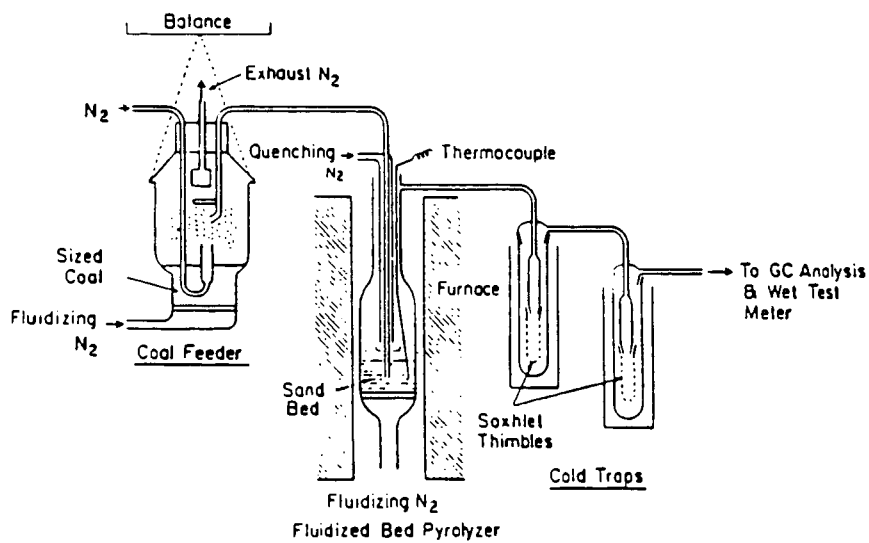
Figure 2

PYROLYSIS BEHAVIOR OF MODEL SULFUR COMPOUNDS
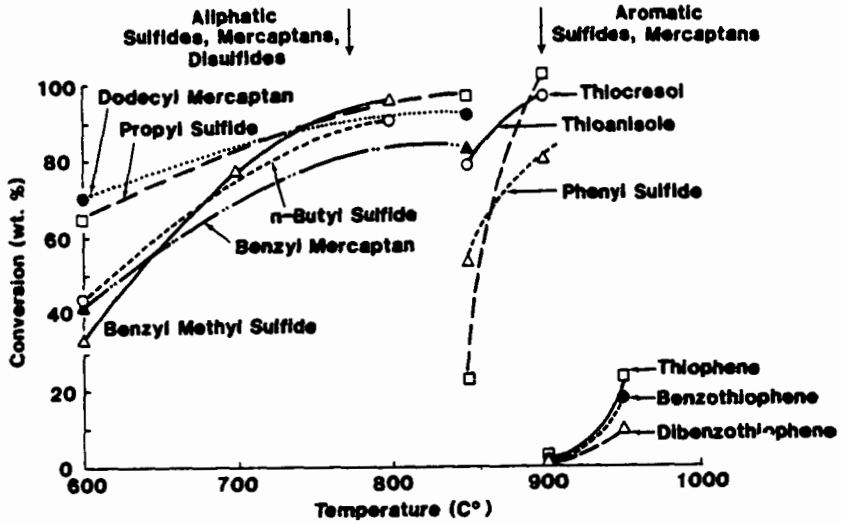0.5 SEC. CONTACT TIME

Figure 3

PYROLYSIS OF PITTSBURGH 8 – R & F
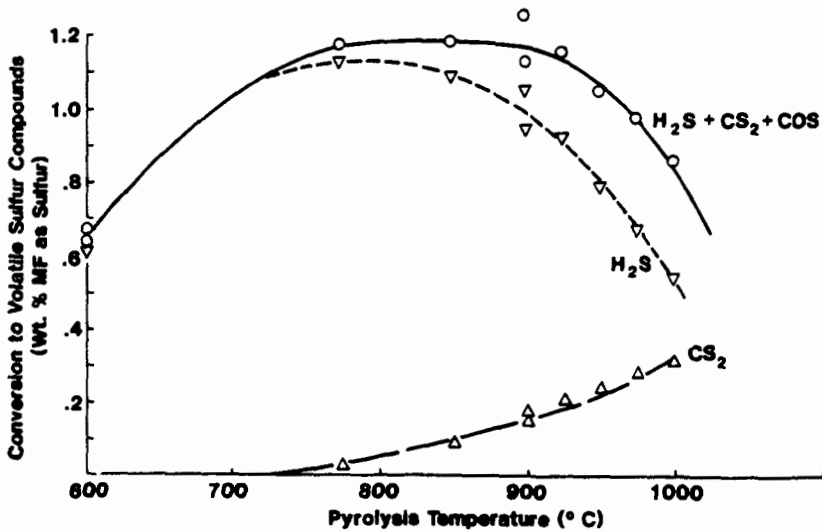YIELD OF VOLATILE SULFUR COMPOUNDS vs TEMPERATURE

463

Figure 4

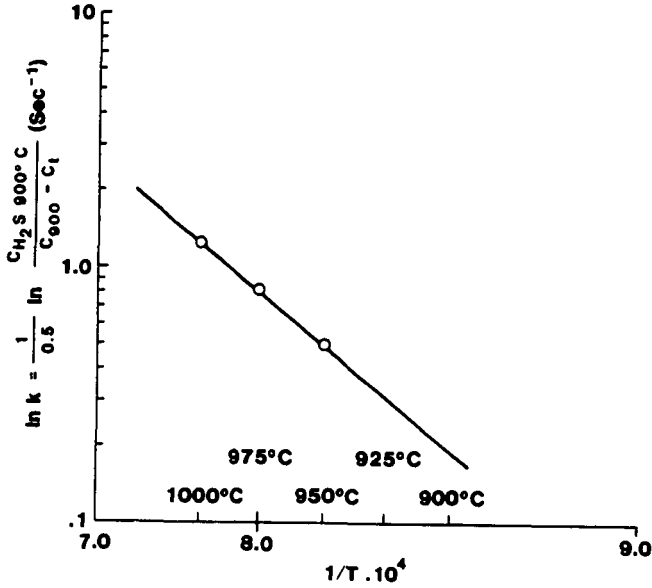## PYROLYSIS OF PITTSBURGH 8 R & F
ARRHENIUS PLOT OF HIGH TEMPERATURE H_2S ABSORPTION

$$\ln k = \frac{1}{0.5} \ln \frac{C_{H_2S}\,900^\circ C}{C_{900} - C_t} \ (Sec^{-1})$$

10

1.0

.1

7.0   8.0   9.0

975°C   925°C

1000°C   950°C   900°C

$1/T \cdot 10^4$

Figure 5

PYROLYSIS OF PITTSBURGH 8 R & F
VOLATILE SULFUR YIELDS vs PYRITE CONCENTRATION

Conversion to Volatile Sulfur Compounds (Wt. % MF as Sulfur)

2.0

1.6

1.2

.8

.4

0

900° C
850° C
775° C

600° C

1.0   2.0   3.0

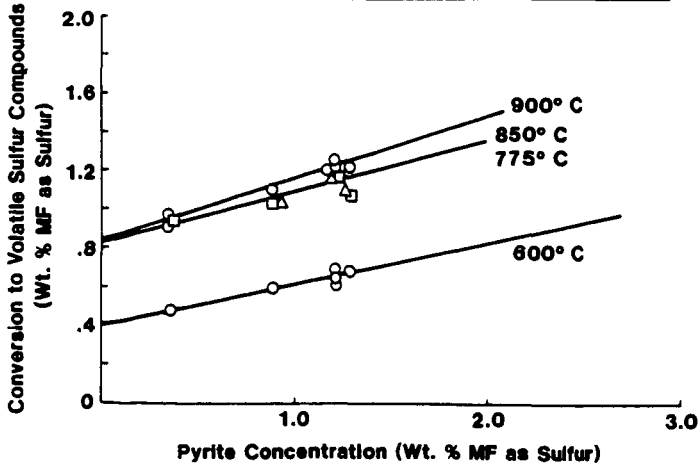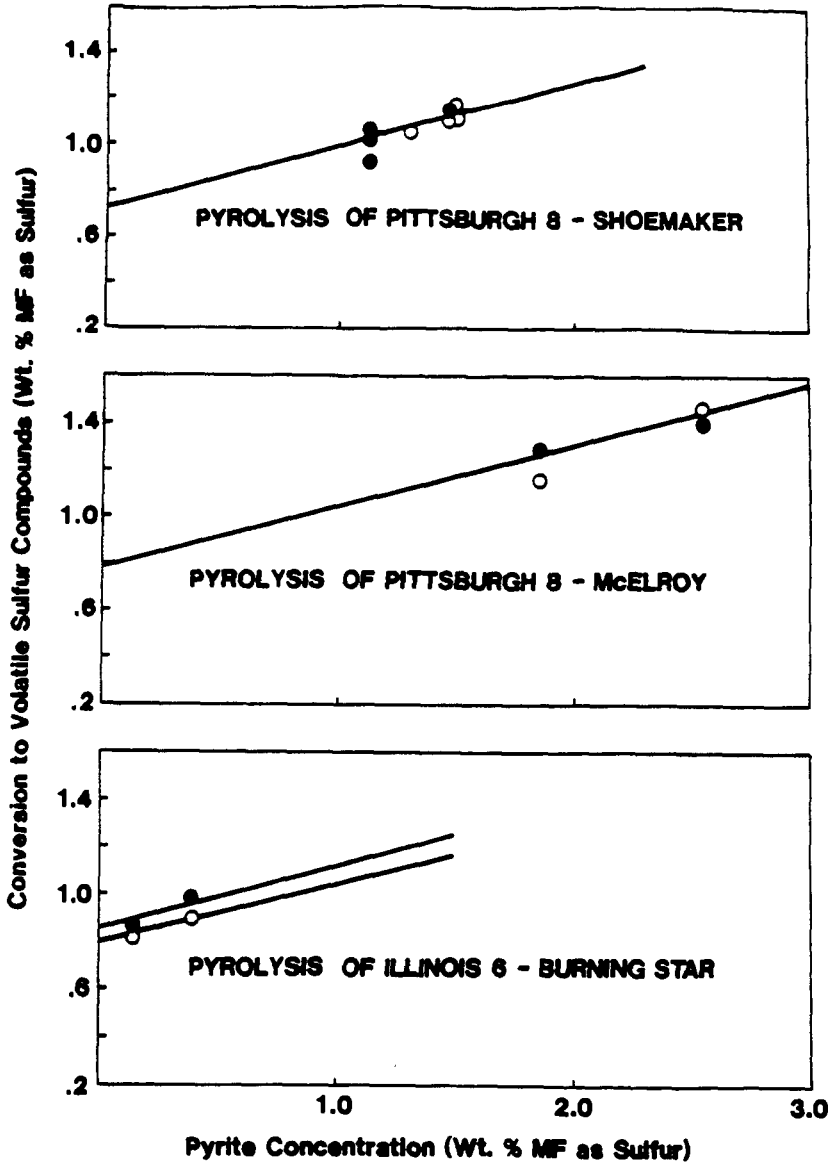Pyrite Concentration (Wt. % MF as Sulfur)

464

Figure 6

VOLATILE SULFUR YIELDS vs PYRITE CONCENTRATION

465

THE EFFECTS OF PYROLYSIS CONDITIONS AND COAL TYPE
ON THE NATURE OF WATER-SOLUBLE ORGANIC EFFLUENTS

Scott F. Ross and Gwen M. Schelkoph

University of North Dakota Energy Research Center
Box 8213, University Station
Grand Forks, North Dakota 58202

Abstract

The effects of pyrolysis conditions and coal type on the nature of water-soluble organic effluents have been investigated using a small pyrolysis reactor with a helium atmosphere at ambient pressure and a sample size of five grams. The reactor is capable of a maximum heating rate of 45°C/min and a maximum furnace temperature of 1100°C. Variables examined include: 1) particle size, 2) maximum temperature, 3) time at temperature, and 4) heating rate. Six coals of various rank were investigated. In addition, three lithotypes of the same coal were examined.

Introduction

The treatment and removal of water-soluble organic effluents from wastewater is an important issue facing coal gasification technology. The extent of treatment is governed by the reuse or environmentally acceptable disposal of the wastewater. Downstream effluent treatment is also dependent on the nature and quantity of tars and water-soluble organics which are produced by pyrolysis and devolatilization reactions in the upper portion of the gasifier. It is desirable to develop a laboratory test to simulate the production of water-soluble organic effluents from a gasifier, thereby eliminating expensive pilot plant tests. Such a test would allow for the prediction of waste composition from specific coals at a variety of operating conditions.

Experimental

A laboratory scale tubular reactor was constructed which allows for the pyrolysis of up to five grams of coal in an inert atmosphere. A Lindbergh split-type furnace with a maximum temperature of 1100°C and programmable heating rate of 5°C/min. to 45°C/min. has been used for heating. A liquid nitrogen cooled trap is used for the collection of water-soluble organic effluents. After completion of the experiment the trap is allowed to warm to above 0°C and the water-soluble organics analyzed by gas chromatography ([1]). The six coals used in this study with their proximate and ultimate analyses are listed in Table I.

Table I. Coal Sample Bank Analysis for Six Coals.

	Indian Head	Gascoyne Blue	Rosebud	Center	Sufco	Illinois Seam No.6
Proximate Analysis, as rec'd; % by wt.						
Moisture	34.0	32.2	25.0	34.7	9.6	2.9
Volatile matter	27.4	34.2	28.6	28.1	33.9	37.3
Fixed carbon*	33.8	17.6	39.2	31.7	48.0	48.6
Ash	4.8	6.0	7.1	5.5	8.5	11.2
Ultimate Analysis maf; % by wt.						
Hydrogen	4.18	5.69	5.11	4.51	5.25	5.54
Carbon	72.03	59.77	76.27	69.97	79.20	77.19
Nitrogen	1.05	0.92	1.28	1.24	1.43	1.61
Sulfur	0.62	1.49	0.93	1.27	0.51	4.59
Oxygen*	22.13	32.12	16.37	23.01	13.61	11.08
Rank	Lig.	Lig.	Subbit.	Lig.	Bit.	Bit.

*By difference.

Results and Discussion

Effect of Coal Type on the Nature of Water-Soluble Organic Effluents

   To develop a correlation between water-soluble organic effluent yields and coal type, six different coals were pyrolyzed in the small pyrolysis reactor (SPR) under identical conditions. The pyrolysis conditions used were a heating rate of 45°C/min., a maximum temperature of 850°C, helium atmosphere, -60 mesh particle size, and a sample size of approximately 5 grams. The data (Table II) indicate water-soluble organic effluent yields to be dependent on coal type, with all products showing significant variation.

Table II. Yields of Water-Soluble Organic Effluents for a Variety of Coal Types.*

Compound	Indian Head	Gascoyne Blue	Rosebud	Center	Sufco	Illinois Seam No. 6
Methanol	1490	730	40	1700	10	40
Acetone	1420	1600	930	1480	750	500
Acetonitrile	230	220	180	280	100	140
2-Butanone	400	510	320	440	250	120
Propionitrile	130	230	90	370	50	40
Phenol	2300	2900	3000	3440	920	1720
o-Cresol	510	590	850	780	390	740
p-Cresol	760	1080	1290	1360	400	950
m-Cresol	710	910	1290	1400	510	1190

*Yields are reported in micrograms/g maf coal.

Effect of Lithotype Composition on the Yields of Water-Soluble Organic Effluents

Several small pyrolysis reactor runs were performed using durain, fusain, and vitrain lithotypes from 8eulah high-sodium (ND) lignite. The pyrolysis conditions used were: a heating rate of 45°C/min., final temperature of 850°C, helium atmosphere and a sample size of approximately five grams. The data (Table III) reveal lithotype-specific variation for most compounds, with the greatest variations in yields being for methanol, acetone, phenol, cresols, and catechol. The vitrain lithotype produced nearly three times the amount of total pyrolysis products as the durain lithotype, suggesting that petrologic analysis of coal samples might be useful in predicting wastewater composition. These results also suggest that petrologic variations within a seam might produce significant variations in wastewater composition as coal mined from different parts of the same seam is gasified.

Table III. Yields of Water-Soluble Organic Effluents for Three Lithotypes.*

Compound	Vitrain	Durain	Fusain
Methanol	2680	580	730
Acetone	1910	1340	1390
Acetonitrile	280	310	270
2-Butanone	480	380	380
Propionitrile	110	160	370
Phenol	2680	1690	3040
o-Cresol	590	340	780
p-Cresol	720	460	850
m-Cresol	680	420	880
Catechol	6940	990	1010

*Yields are reported in micrograms/g maf coal.

Correlation of Yields of Water-Soluble Organic Effluents to Coal Parameters

It is the ultimate goal of this project to develop a series of equations which will predict wastewater composition from a gasifier based, in part, on certain coal parameters easily determined in the laboratory. Relationships have been found which correlate the yields of three pyrolysis products, methanol, 2-butanone and acetone, to coal-specific data which is readily available.

Methoxy content determinations (2) have been made for eleven different samples tested in the small pyrolysis reactor. These samples include whole coals as well as individual lithotypes. The methoxy contents of the lithotypes were plotted versus the yield of methanol generated during pyrolysis to 850°C. A linear least squares fit of the data resulted in a correlation coefficient of 0.95.

The yields of 2-butanone and acetone were plotted versus carbon/oxygen ratios for six coals pyrolyzed in the small pyrolysis reactor. A linear least squares fit of the data gave a very good fit for both compounds (Figure 1 and Figure 2). 2-Butanone and acetone both had correlation coefficients of 0.99.

Future work will focus on the identification of further relationships which will attempt to correlate pyrolysis yields of the remaining six compounds with other coal parameters.

Effect of Pyrolysis Conditions on the Nature of Water-Soluble Organic Effluents

Effect of Particle Size. In order to determine the effect of particle size on the yield of water-soluble organic effluents, the pyrolysis products from -60 mesh coal were compared to the products from 1/2 inch particles for Rosebud (MT) coal. The pyrolysis conditions were a heating rate of 45°C/min., final temperature 850°C, and a helium atmosphere. The effect of particle size was negligible; the yield of water-soluble organic effluents was independent of the size of the coal particle which generated those effluents (Table IV). However, it is advantageous to use riffled -60 mesh coal particles in most experiments in order to avoid inhomogeneity in the coal sample, which would result in anomalous effluent yields.

Table IV. Effect of Coal Particle Size on the Nature of Water-Soluble Organic Effluent.*

Compound	Rosebud	
	-60 mesh	1/2 inch
Methanol	40	30
Acetone	930	890
Acetonitrile	180	160
2-Butanone	320	320
Propionitrile	90	30
Phenol	3000	2810
o-Cresol	850	850
o-Cresol	1290	1220
m-Cresol	1290	1230

*Reported as micrograms/g maf coal.

Effect of Maximum Temperature. To determine the effect of maximum temperature on the yield of water soluble organic effluents, Indian Head (ND) lignite was pyrolyzed at two final temperatures: 850° and 1100°C. The pyrolysis conditions used were a heating rate of 45°C/min., -60 mesh particle size, and a sample size of approximately 5 grams. A comparison of the yield data (Table V) for these two runs revealed the yields of methanol, acetone, acetonitrile, 2-butanone and propionitrile to be similar. However, the increased yields of phenol and cresols at 1100°C suggest that the evolution of water-soluble organics is not complete at 850°C. Model studies indicate that phenol and cresols generated at the lower temperatures evolve from alkyl-aryl ether precursors (3). The increase in phenol and cresol yields at 1100°C may result, in part, from the cleavage of diaryl ethers with their relatively higher carbon-oxygen bond energies.

Table V. Effect of Maximum Temperature on the Nature of Water-Soluble Organic Effluents.

Compound	Micrograms/g maf coal	
	850°C	1100°C
Methanol	1490	1460
Acetone	1420	1490
Acetonitrile	230	240
2-Butanone	400	400
Propionitrile	130	90
Phenol	2300	3220
o-Cresol	510	740
p-Cresol	760	1120
m-Cresol	710	1270

Effect of Time at Temperature. Indian Head (ND) and Rosebud (MT) coals were subjected to zero and 30 minute isothermal periods at maximum temperatures of 380°C and 850°C to determine the effect of time at temperature ("residence time") on pyrolysis yields for water-soluble organics. The pyrolysis conditions were a heating rate of 45°C/min., a helium atmosphere, and a sample size of approximately 5 grams. The effect of residence time on the yields of water-soluble organics (Table VI) was substantial at 380°C. With no isothermal period, the yield of products was below the gas chromatograph's threshold for accurate quantification. At the higher temperature the effect of residence time was quite small and in the case of the Indian Head lignite nonexistent.

Table VI.   Effect of Time at Temperature on the Nature of Water-Soluble Organic Effluents.*

| | Maximum Temperature 380°C | | | |
| | Indian Head | | Rosebud | |
Compound	0 min.	30 min.	0 min.	30 min.
Methanol	**	900	**	20
Acetone	**	480	**	300
Acetonitrile	**	30	**	10
2-Butanone	**	140	**	130
Propionitrile	**	**	**	10
Phenol	**	1370	**	540
o-Cresol	**	350	**	120
p-Cresol	**	550	**	230
m-Cresol	**	450	**	170
Catechol	**	1480	---	---

| | Maximum Temperature 850°C | | | |
| | Indian Head | | Rosebud | |
Compound	0 min.	30 min.	0 min.	30 min.
Methanol	1490	1740	40	30
Acetone	1420	1460	930	840
Acetonitrile	230	240	180	170
2-Butanone	400	370	320	280
Propionitrile	130	270	90	20
Phenol	2300	2360	3000	2690
o-Cresol	510	530	850	800
p-Cresol	760	820	1290	1080
m-Cresol	710	820	1290	1140
Catechol	2210	2120	---	---

*Reported in micrograms/g maf coal.
**Below instrument threshold for accurate quantification.
---Not determined.

Effect of Heating Rate.   To determine the effect of heating rate on the yield of water-soluble organic effluents, pyrolysis of Center Mine (ND) lignite was carried out at 380°C and 850°C using heat rates of 5°C/min. and 45°C/min. Both the 380°C data and the 850°C data (Table VII) reveal a higher yield for phenol and cresols at the slower heating rate. This could be due to the relative length of the experiments; the fast heating rate experiment takes approximately 20 minutes, whereas the slow heating rate experiment takes 170 minutes. It is possible that the effect that is being observed is not so much heating rate as it is time at temperature ("residence time").

Table VII. Effect of Heating Rate on the Nature of Water-Soluble Organic Effluents.*

Compound	380 Maximum Temp.		850 Maximum Temp.	
	5°C/min.	45°C/min.	5°C/min.	45°C/min.
Methanol	570	270	1590	1700
Acetone	110	40	1190	1490
Acetonitrile	**	**	300	280
2-Butanone	20	10	310	440
Propionitrile	**	**	30	380
Phenol	460	100	4380	3460
o-Cresol	50	10	1300	780
p-Cresol	180	40	1740	1360
m-Cresol	80	10	1920	1400

*Results are reported in micrograms/g maf coal.
**Below instrument threshold for accurate quantification.

Conclusion

A laboratory scale tubular reactor test is able to differentiate between the relative yields of several water-soluble organic effluents produced during pyrolysis for a variety of coals under differing pyrolysis conditions. Correlations between pyrolysis yields and certain coal parameters for three of the compounds examined have been developed which allow for the prediction of pyrolysis yields for these compounds for as yet untested coals.

Acknowledgment

Literature Cited

1. Olson, E.S. and J.W. Diehl, 186th ACS National Meeting, Washington, D.C., Abstracts of Papers, Anyl 63, (1983).

2. Olson, E.S. and J.W. Diehl, Quarterly Technical Progress Report for the Period October-December 1984, University of North Dakota Energy Research Center, in print.

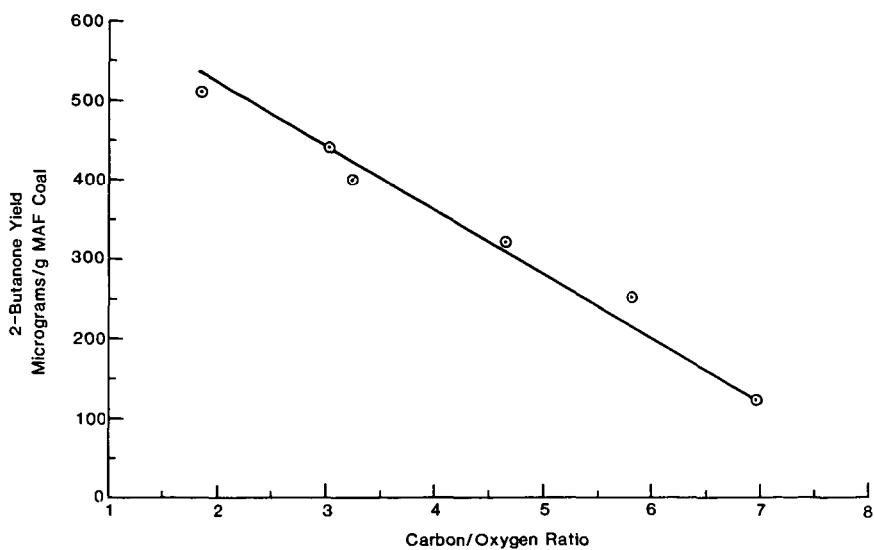3. Siskin, Michael and Thomas Aczel, Fuel, 62, 1321 (1983).

Figure 1. Correlation of 2-butanone yields to carbon/oxygen ratio for the six coals listed in Table I.
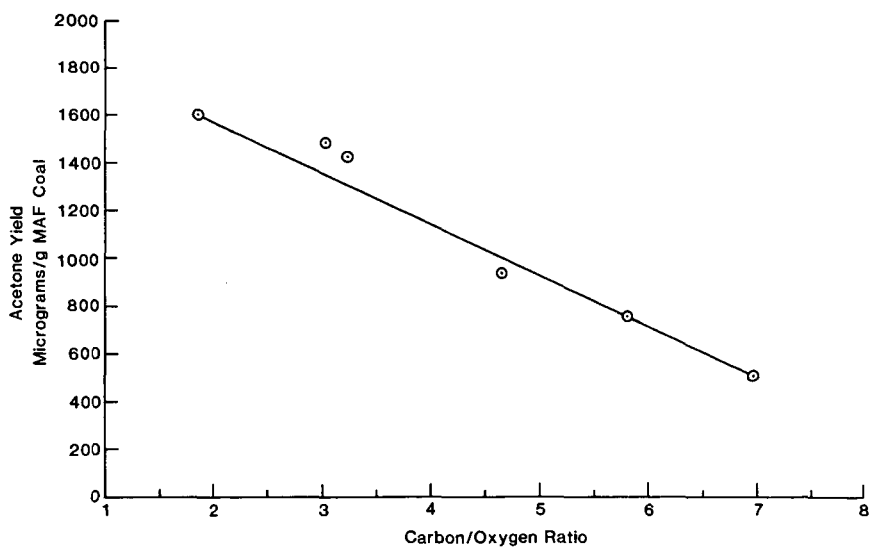

Figure 2. Correlation of acetone yields to carbon/oxygen ratio for the six coals listed in Table I.

Selective Removal of Nitrogenous Compounds Using Zeolites

G. Jean, E. Bonvie, and H. Sawatzky

Energy Research Laboratories (CANMET)
555 Booth Street
Ottawa, Ontario, Canada
K1A 0G1

Introduction
    Various sorbents have been used in the past for the selective removal of nitrogenous compounds. Supported ferric chloride (1), macroreticular ion exchange resins (2-4), basic and neutral alumina (5), and acid modified silica (6) can selectively remove nitrogenous compounds from petroleum fractions. These separation methods however were designed for small scale analytical separation. Recently there has been some interest in large scale separation of nitrogenous material (7-9). This interest stems from the possibility of using an adsorption (or sorption) process as a substitute for the expensive hydrotreating process.
    This paper describes the selective removal of nitrogenous compounds from naphthas using zeolites. The selectivity was determined for several zeolites using a model compound solution. The selectivity strongly depends on the nature of the compound. The zeolite was cation exchanged in order to modify the selectivity.

Experimental
    The model compound solution was prepared by dissolving the appropriate amount of compound in reagent grade toluene. The composition of the two solutions are given in Table 1.
    The zeolites obtained from BDH Chemicals were shaken over night in a 1M aqueous solution. The chloride salt of the cation to exchange was used. The zeolite was then filtered, washed, and dried at 110°C for 12 h. The zeolite was activated at 520°C in the presence of air for 12 h.
    A typical experiment involved pumping the feed continuously at 0.5 mL/min into a 30 cm long and 0.4 cm I.D. stainless steel column packed with the sorbent. Samples of the effluent were collected every 5 mL and subsequently analyzed using a Varian 6000 gas chromatograph equipped with a 30 m long DB-5 capillary column. For whole naphthas the effluent samples were analysed for total nitrogen by chemiluminescence using a Dohrman total nitrogen analyzer. All experiments were performed at room temperature. Three grams of zeolite was used for each run. Table 2 give the properties of the naphthas used in this study.

Results and discussion
    The sorption results for model solution 1 by zeolite 13 X in the sodium form are shown in Fig. 1. These results clearly show that the degree of sorption depends on the nature of the compound. Compounds such as benzacridine and tetrahydrocarbazole appear in the effluent after 20 mL whereas compounds such as benzylamine are still completely removed after 150 mL. There is an inverse correlation between the amount sorbed and the molecular size of a compound; the amount of three- and four-ring compounds sorbed is generally lower than that of two- and one-ring compounds. The relation between separation and molecular size is well documented (10-11); zeolites are known as shape selective sorbents because of their uniform pore size. Smaller pore size zeolites were tested using solution 1. The efficiency of separation was proportional to pore size.

The previous results indicate the difficulty of removing all nitrogenous compounds indiscriminately. The separation is diffusion-controlled and larger molecules are not removed to any great extent. The model compound study suggests that zeolites would be most effective for the treatment of naphthas which contain small nitrogenous compounds. An experiment was therefore carried out using zeolite 13X and two naphthas (Fig. 2). Using the area over the breakthrough curve the sorption capacities were calculated. The capacities were: 4.61 mg N (1.36 mg N/g zeolite) for the coker naphtha, and 14.24 mg N (4.3 mg N/g zeolite) for the hydroprocessed naphtha which is significantly lower than the 298 mg (100 mg N/g zeolite) obtained for the model compound solution 1 and the 332 mg obtained for model compound solution 2. Solution 2 is more representative of a naphtha since it contains smaller nitrogenous compounds than solution 1. Both solutions give a capacity of 10% by weight of zeolite.

The sorption capacity for the model compounds is similar to that obtained for vapour phase sorption of hydrocarbons and nitrogenous bases. Breck and Flanagen obtained a capacity of 0.227 g of tributylamine per gram of zeolite X at room temperature (12). In a liquid phase experiment $C_8F_{18}O$ was separated from $(C_4F_9)_3$ N by sorption on a zeolite 13X; the $C_8F_{18}O$ loading at breakthrough was 0.3 g/g of zeolite (13). The capacity obtained in this study demonstrates the possibility of using zeolites for large scale separation. The lower capacity obtained for naphthas suggests the competitive sorption of non-nitrogenous compounds; the sorbent may not be totally selective for nitrogenous compounds and substantial quantities of olefins or aromatics may be sorbed. No direct evidence for this is presented in this study. These aspects are presently under study. The aim is to improve the selectivity for nitrogenous compounds, specifically for multi-ring compounds.

The selectivity shown by a sorbent toward a sorbate is determined by several types of interaction energies such as dispersion, repulsion, polarization, and dipole/quadrupole interactions. For a given feed the selectivity is a function of the nature of the cation in the zeolite, the surface acidity and the sorbent pretreatment. For instance, large pore size zeolites such as 13X exhibit selectivity for the aromatic components of mixture of aromatics and paraffins. Replacing the polarizing cation by protons reverses the selectivity (14). Similarly in this study the cation of zeolite 13X (sodium) was replaced by other cations, namely H, Zn, Co in order to see the effect on selectivity. The objective is to find two zeolite forms that complement each other. The results are presented in Tables 3-6.

The substitution of the cation changes the selectivity considerably; for instance the capacity of the sodium form for aniline is over 50 mg whereas that of the hydrogen and the zinc forms is 10 and 14 mg respectively. Similarly the capacity of the sodium and hydrogen forms for cyclohexylamine is 50 mg and is only 10 mg for the zinc form. Other compounds such as 1,2,5-trimethylpyrrole are not affected by the exchange. These results suggest the possibility of using two zeolites that complement each other to improve the efficiency of separation. For instance the sodium and hydrogen form seems to be the best combination. Indeed the sodium form is most effective to remove aniline, benzylamine, cyclohexylamine, and to a lesser extent ethylamine but is unable to remove trimethylpyrrole, decylamine, and octylamine. The hydrogen form is most effective to remove decylamine, octylamine, and cyclohexylamine but unable to remove aniline. Such a combination has not been tested in this study.

Conclusion

This study demonstrates the possibility of using zeolites for the large scale selective removal of nitrogenous compounds from petroleum fractions. The results indicate the difficulty of removing all nitrogenous compounds indiscriminately. Larger neutral compounds are not removed to any great extent while smaller basic compounds are removed extensively. This deficiency can be corrected somewhat by modifying the selectivity of the zeolite by cation exchange.

Zeolites were also found to be effective for the selective removal of nitrogenous compounds contained in naphthas. The sorption capacity obtained with naphthas is much lower than expected based on the model compound study. This suggests that non-nitrogenous compounds are competing for the surface sites. More data will be required to identify the competing species and modify the zeolite to inhibit this phenomenon.

References

1) D.M. Jewel and R.E. Snyder, J. Chromatog. 38,351 (1968)
2) D.M. Jewel, J.H. Weber, J.W. Bunger, H. Plancher, and D.R. Latham, Anal. Chem. 44, 139 (1972)
3) D.E. Hirsh, R.L. Hopkins, H.J. Coleman, F.O. Cotton and C.J. Thompson Anal. Chem. 44, 915 (1972)
4) H. Sawatzky, A.E. George, G.T. Smiley, and D.S. Montgomery, Fuel 55, 16 (1976)
5) C.D. Ford, S.A. Homes, L.F. Thompson and D.R. Latham, Anal. Chem. 55, 831 (1981)
6) J.M. Schmitter, I. Ignatiadis, P. Arpino and G. Guiochon, Anal. Chem. 55, 1685 (1983)
7) G. Jean, E. Bonvie and H. Sawatzky, Separ. Scien. Tech., submitted for publication
8) C.A. Audeh, Ind. Eng. Chem. Prod. Res. Dev., 22, 276 (1983)
9) H.W. Coi and M.B. Dines, Fuel 64,4 (1985)
10) D.W. Breck "Zeolite molecular sieves: structure, chemistry, and use" John Wiley and Sons, London, 1974
11) W.M. Meier and S.B. Uytterhoeven, Ed. "Molecular sieves" American Chemical Society, Washington, D.C. 1973, Advances in Chemistry Series, No. 121
12) D.W. Breck and E.W. Flanagen, "Molecular Seives", Society of Chemical Industry, London, 1968, p. 47
13) B.J. Mair and M. Shamaiengen, Anal. Chem., 30, 276 (1958)
14) P.E. Eberly, Ind. Eng. Chem. Prod. Res. Develop., 10, 433 (1971)

Table 1 - Composition of model solutions

Solution 1		Solution 2	
Compound	ppm N	Compound	ppm N
aniline	30.12	aniline	48.07
1,2,5-trimethylpyrrole	28.20	3-ethylpyridine	48.22
benzylamine	39.79	4-ethylpyridine	49.05
n-octylamine	32.79	n-octylamine	44.40
n-decylamine	27.08	n-decylamine	35.95
quinoline	32.02	1,2,5-trimethylpyrrole	50.76
indole	29.37	cyclohexylamine	54.41
3-methylindole	26.74	benzylamine	51.21
2,2´-dipyridyl	55.58	2,4,6-collidine	48.26
1-phenethylpiperidine	22.88	tri-n-propylamine	34.49
2-phenylpyrydine	24.26	tert-butylamine	51.85
dibenzylamine	26.48		
tetrahydrocarbazole	27.70		
carbazole	25.24		
2-methylacridine	19.40		
3,4-benzacridine	7.85		
2-aminochrysene	13.90		
phenothiazine	29.60		
Total N concentration	518.21		516.67

Table 2 - Naphtha properties

Hydroprocessed	Coker	
Specific gravity 60/60 F	0.74	0.75
Sulphur wt %	0.18	0.18
Carbon wt %	85.98	85.25
Hydrogen wt %	13.45	13.88
Nitrogen wt %	0.005	0.002
Bromide number	24	74
Simulated distillation (wt %)		
Paraffins	55	24.61
Olefins	15	61.79
Naphtenes	19	0.0
Aromatics	10	13.60

Table 3 - Selectivity for zeolite 13X in the sodium form (Na)

Compound	Volume at breakthrough (mL)	Total loading (mg)
1,2,5-trimethylpyrrole	22	12.16
n-decylamine	82	23.23
tri-n-propylamine	82	26.00
n-octylamine	105	30.93
2,4,6-collidine	105	42.76
3-ethylamine	144	47.07
4-ethylamine	160	51.66
cyclohexylamine	162	53.91
tert-butylamine	183	44.77
aniline and benzylamine not broken through		
Total		332.49

Table 4 - Selectivity for zeolite 13X in the hydrogen form (H)

Compound	Volume at breakthrough (mL)	Loading at breakthrough (mg)
aniline	36	9.98
1,2,5-trimethylpyrrole	36	11.74
3-ethylpyridine	45	14.31
4-ethylpyridine	48	15.92
2,4,6-collidine	60	21.29
tri-n-propylamine	78	23.64
n-decylamine	97	32.13
n-octylamine	123	43.56
benzylamine	135	45.85
cyclohexylamine	148	49.09
tert-butylamine not broken through		
Total		267.51

Table 5 - Selectivity for zeolite 13X in the zinc form (Zn)

Compound	Volume at Breakthrough (mL)	Loading at Breakthrough (mg)
cyclohexylamine	20	6.80
1,2,5-trimethylpyrrole	42	12.47
aniline	48	13.83
3-ethylpyridine	56	18.23
tri-n-propylamine	68	20.88
2,4,6-collidine	72	26.31
n-decylamine	74	26.29
4-ethylpyridine	78	25.95
n-octylamine, tert-butylamine, and benzylamine not broken through		
Total		150.76

Table 6 - Selectivity for zeolite 13X in the cobalt form (Co)

Compound	Volume at Breakthrough (mL)	Loading at Breakthrough (mg)
aniline	16	3.65
1,2,5-trimethylpyrrole	16	4.91
2,4,6-collidine	18	5.28
3-ethylpyridine	18	5.43
4-ethylpyridine	23	7.04
tri-n-propylamine	24	7.37
n-decylamine	67	22.89
n-octylamine	74	25.20
benzylamine	75	25.64
cyclohexylamine	79	27.13
tert-butylamine not broken through		
Total		134.54
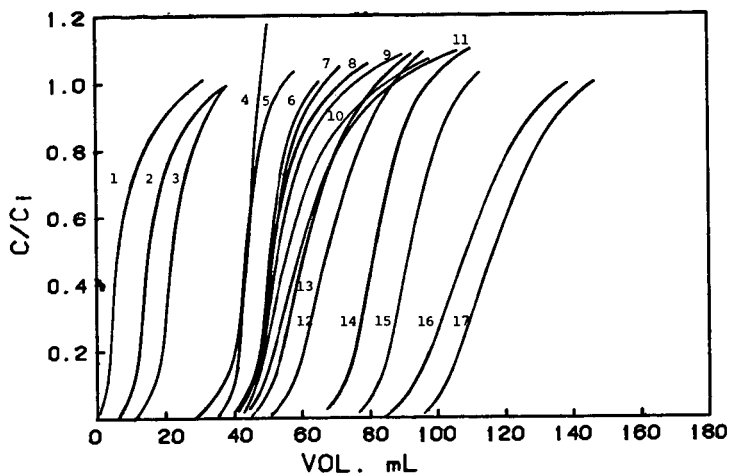
FIGURE 1 – Selectivity of sorption of zeolite 13X for a standard mixture.
1) benzacridine, 2) 1,2,5-trimethylpyrrole, 3) tetrahydrocarbazole,
4) n-decylamine, 5) 2-methylacridine, 6) aminochrysene, 7) carbazole
8) n-octylamine, 9) 1-phenethylpiperidine, 10) phenothiazine,
11) 2-phenylpyridine, 12) 3-methylindole, 13) dibenzylamine,
14) Indole, 15) quinoline, 16) aniline, 17) 2,2' dipyridyl.
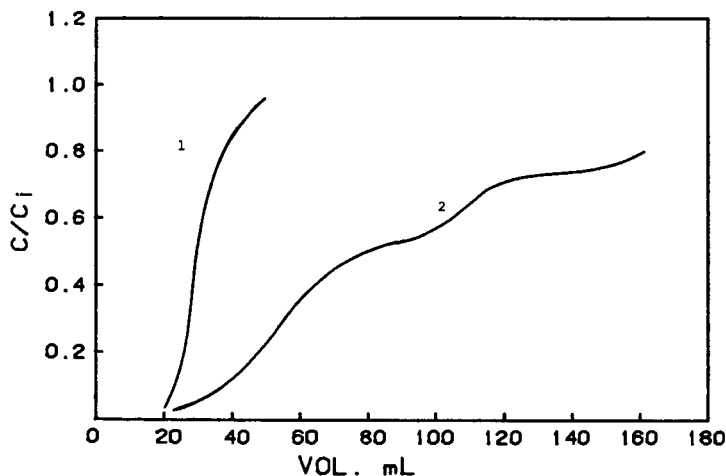Benzylamine did not elute after 150 mL.

·Fig. 2 – Breakthrough curve for: hydroprocessed naphtha (curve 1)
and coker naphtha (curve 2) sorbed on zeolite 13X.

480

ARRHENIUS ACTIVATION ENERGIES OF THE REACTION OF LOW-RANK COAL CHARS AND STEAM

R.C. Timpe, S.A. Farnum, S.J. Galegher,
J.G. Hendrikson and M.M. Fegley

University of North Dakota Energy Research Center
Box 8213, University Station
Grand Forks, North Dakota 58202

Introduction

The chemical reaction between coal char and steam to produce synthesis gas, CO and H_2, is well known. These products can be used directly as low-heating-value gas or as precursors for the catalytic synthesis of methanol and ammonia, oxo compounds, methane and petroleum substitutes. More recently, however, interest has centered on producing the gas for its hydrogen content. The hydrogen can be purified for use as a fuel.

The rate of the reaction involving char and steam is increased markedly by the use of catalysts, particularly alkali metal compounds (1-3). Potassium carbonate, which is commonly recognized as the best alkali catalyst for this reaction (4), was chosen as the catalyst to use in examining the gasification of chars prepared from Indian Head and Velva North Dakota lignites, and Wyodak Wyoming subbituminous coal. These three low-rank coals were converted to chars and then reacted with steam at 700°, 750° and 800°C both with and without K_2CO_3 catalyst. The course of the reaction was followed by thermogravimetric analysis (TGA). Sodium carbonate was also used to catalyze the Velva and Indian Head char-steam reactions. Sodium carbonate is a less expensive material than K_2CO_3 and, if shown to be an effective catalyst in place of K_2CO_3, could reduce considerably the cost of the conversion process.

This paper reports the apparent Arrhenius energies of activation (Ea) and pre-exponential factors (A) for the steam gasification of the uncatalyzed and K_2CO_3-catalyzed Velva, Indian Head, and Wyodak coal chars, and the Na_2CO_3-catalyzed Velva and Indian Head coal chars.

Experimental

The three low-rank coals and their composition are shown in Table I.   Table II shows the experiment matrix. Each coal was ground to 100 x 140 mesh and a portion of the ground coal was mixed intimately with 10 wt% dry K_2CO_3 or Na_2CO_3 for the catalyst tests.   The coals in both the uncatalyzed and catalyzed form were devolatilized and then reacted with steam in a Du Pont 951 Thermo-gravimetric Analyzer (TGA) interfaced with a Du Pont 1090 Thermal Analyzer. The devolatilization removed the moisture and the volatile matter from the coal and produced the char containing the active fixed carbon for the steam-carbon reaction.

(a) Devolatilization.
Approximately 20 mg of uncatalyzed or catalyzed coal was loaded on the sample pan of the thermogravimetric analyzer. A flow of 275 mg/min Argon was passed through the reaction chamber during the devolatilization of the coal. The sample was heated at 100°C/min to one of three temperatures, 700°, 750°, or 800°C. After the target temperature was achieved, isothermal heating at that temperature was continued until at least 15 minutes total time had elapsed. The resulting char was held under flowing argon without cooling until the char-steam reaction was initiated.

(b) Char-Steam Reaction.
     Steam was introduced through a side-arm of the quartz furnace tube at a rate of 1-6 mg/min. The argon flow was reduced to 100 mg/min during the steam reaction. As the reaction proceeded, the loss of weight was recorded at the rate of one data point every two seconds until the char reached constant weight. The rate parameter, k, was calculated from the data obtained and the energy of activation (Ea) was calculated from the plots of ln k verses 1/T for the three reaction temperatures.

Table I. Low-Rank Coal Composition.

	Indian Head	Velva	Wyodak
Proximate Analysis (AR) wt%:			
Moisture	36.62	38.8	30.99
Volatile Matter	26.07	25.3	30.43
Fixed Carbon	30.50	29.0	32.96
Ash	6.81	6.9	5.62
Ultimate Analysis (MAF) wt%:			
Carbon	70.4	70.4	73.7
Hydrogen	5.45	5.30	5.38
Nitrogen	1.40	1.40	1.22
Oxygen (by diff)	21.7	22.3	19.1
Sulfur	1.04	0.60	0.53
Ash Analysis (wt% of ash):			
SiO_2	26.25	19.6	28.0
Al_2O_3	10.73	12.7	15.0
Fe_2O_3	14.03	5.8	4.30
TiO_2	0.53	0.40	1.20
P_2O_5	0.42	0.60	1.50
CaO	15.95	36.0	21.7
MgO	4.88	10.20	6.60
Na_2O	7.97	2.10	1.60

Table II. Reaction of Devolatilized Coal Char With and Without 10 wt% Catalyst.

Reaction Temp., °C	700			750			800		
Catalyst	None	K_2CO_3	Na_2CO_3	None	K_2CO_3	Na_2CO_3	None	K_2CO_3	Na_2CO_3
Coal Reacted:									
Indian Head	X	X	X	X	X	X	X	X	X
Velva	X	X	X	X	X	X	X	X	X
Wyodak	X	X		X	X		X	X	

Results and Discussion

Preliminary experiments were conducted to determine optimum operating parameters for the reaction on the TGA. It was determined that a catalyzed or uncatalyzed low rank coal sample size of ~20 mg produced a satisfactory quantity and quality of char when devolatilized according to the procedure discussed previously. The devolatilization appeared to be complete after about ten minutes. The temperature was maintained for a minimum of an additional five minutes to ensure uniformity in carrying out the devolatilization step. The char was held at that temperature and the steam flow was started. Steam flow rates of 0.5 to 200 mg/min were investigated in preliminary experiments to allow selection of a suitable rate. The flow rate, optimized at 1-6 mg/min, supplied steam at a rate sufficient to feed the reaction without showing signs of diffusion limitation and without causing condensation build-up on the cool parts of the balance. When excess steam flow caused condensation to collect on the unheated parts of the balance arm or on the electrical contacts of the balance or thermocouple, the instrument response became erratic.

When the optimum reaction conditions had been determined, all experiments were run in at least duplicate with excellent reproducibility, and reactivity parameters were averaged for use in calculating Ea and A. Since, in some experiments up to 10 % of the calculated weight of the fixed carbon did not react, 90% conversion was considered complete for interpreting data shown in Figure 1 and 2.

The reactions between uncatalyzed coal char and steam for each of the three coals when carried out at 750°C, showed that 90% conversion of char (fixed carbon) was most rapid in the Velva lignite (Figure 1). Ninety percent of Indian Head and Wyodak char conversion occured at slower rates, with Wyodak being the slower as expected because of its higher rank (5).

Loading of 10 wt% K_2CO_3 catalyst gave the data plotted in Figure 2. Velva lignite chars achieved 90% conversion much more rapidly than any of the other chars tested.

The catalyst loading of 10 wt% Na_2CO_3 on Indian Head and Velva lignites was investigated and compared with the results from K_2CO_3 catalysis (Figures 3 and 4). The catalytic effect of 10 wt% Na_2CO_3 was nearly identical on a weight-to-weight basis to that of the K_2CO_3 up to 90% conversion for the Velva coal. It appeared to be slightly better than K_2CO_3 on a weight-to-weight basis for catalyzing the Indian Head char reaction. On a molar basis, however, K_2CO_3 was better for catalysis of both coal chars.

Uncatalyzed and K_2CO_3-catalyzed coal char-steam reactions were also carried out at 700° and 800°C at the 10% catalyst loading. Mahajan, et. al., determined that a very useful parameter for correlating char reactivity data is the time needed to reach a fractional burn-off of 50% of the char (7). The reactivity parameter, K, was calculated from the conversion rate data at 700°, 750°, and 800°C based on weight of char sample reacted at 50% of fixed carbon versus time. Arrhenius plots of ln $k_{0.5}$ versus 1/T were prepared (6), and Ea was calculated from the slope of the line, and A was determined from the Y-intercept (Figures 5, 6, and 7). These values are listed in Table III. For chars from Velva, Indian Head and Wyodak low-rank coals, the addition of K_2CO_3 decreased the apparent Ea by as much as 60% that of the uncatalyzed coal char. For equal wt% catalyst loading Na_2CO_3 was found to be at least as effective as K_2CO_3 in catalyzing the Velva and Indian Head char conversion. On a molar basis however the sodium catalyst would contain 1.30 times as many metal cations as the potassium catalyst when the coals are loaded with equal weights of the two catalysts. Although the Na_2CO_3 may not be as active atom for atom as K_2CO_3, it was as effective in lowering the apparent energy of activation of the two lignites on a weight-for-weight basis and is much less expensive.

Table III. The Apparent Energies of Activation and Pre-exponential Factors Calculated from Arrhenius Plots at 0.5 of Fixed Carbon.

	Indian Head		Velva		Wyodak	
	Ea*	A**	Ea	A	Ea	A
As-received	28.8	1.78×10^6	29.8	4.11×10^6	31.8	7.67×10^6
K_2CO_3 catalyzed	18.4	4.26×10^4	11.5	1.85×10^3	21.1	1.86×10^5
Na_2CO_3 catalyzed	15.9	1.31×10^4	11.9	2.25×10^3	--	--

 * Kcal/mole fixed carbon
** /hr

   A few selected examples of apparent energies of activation from recent literature are shown in Table IV. Serageldin and Pan have suggested that the apparent energies of activation for the decomposition of coal change with operating conditions indicating that more than one mechanistic route is available (1). The data in Tables III and IV suggest that although coal rank is a factor in determining the reactivity of coal char and consequently E_A other factors such as time and temperature involved in char preparation, the quantity and type of mineral material in the coal, the gas content and composition as well as type and amount of catalyst have an effect on the value of E_A and A (1, 2, 8-10).

Table IV. Selected Literature Values of Apparent Energies of Activation.

Coal	Rank	Atmosphere	Catalyst Loading	Temp. Range (K)	E_A	Ref.
Illinois No.6	Bit	He/Steam	5% Na (as Na_2CO_3)	873-1023	30.5	8
		He/Steam	10% Na (as Na_2CO_3)	873-1023	24.5	8
Wyodak	Subbit	He/Steam	5% K (as K_2CO_3)	873-973	44.8	1
		He/Steam	10% K (as K_2CO_3)	873-973	39.1	1
Inland Mine	Subbit	N_2		723-823	12.0	2
		N_2		938-1223	16.1	2
		N_2	4% Na (as Na_2CO_3)	723-823	11.0	2
		N_2	4% Na (as Na_2CO_3)	938-1223	15.4	2
		N_2	4% K (as K_2CO_3)	723-823	11.5	2
		N_2	4% K (as K_2CO_3)	938-1223	13.6	2
PSOL-91	Lignite	N_2-Steam		1023-1163	42.1	5

Literature Cited

1. Veraa, M.J., and A.T. Bell, Fuel, 1978 <u>57</u> 194.
2. Serageldin, M.A., and Wei-Pring Pan, "Coal Analysis Using Thermogravimetry", Thermochimica Acta, 1984, 76, 145-160.
3. Radovic, L.R., P.L. Walker, Jr., R.G. Jenkins, Fuel, 1984, <u>63</u>, 1028.
4. Tomita, A., Y. Ohtsuka and Y. Tamai; Fuel, 1983, <u>62</u>, 150.
5. Liwares-Solano, A., O.M. Mahajaw, P.L. Walker, Jr., Fuel, 1979 <u>58</u>, 327.
6. Levine, I.N., "Physical Chemistry", 1978, 1st Ed., 498-502.
7. Mahajan, O.P., R. Yarzab, P.L. Walker, Jr., Fuel, 1978, <u>57</u>, 644.
8. Yuh, S.J., E.E. Wolf, Fuel, 1984, <u>63</u>, 1604.
9. Tomita, A., O.P. Mahajan, P.L. Walker, Jr., Fuel, 1977, <u>56</u>, 137.
10. Jenkins, R.G., S.P. Nandi, P.L. Walker, Jr., Fuel, 1973, <u>52</u>, 288.
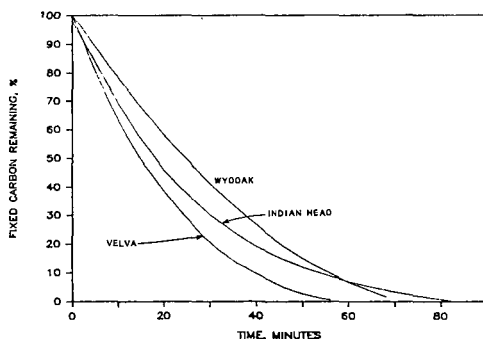
Figure 1. Uncatalyzed steam gasification - carbon conversion at 750°C.
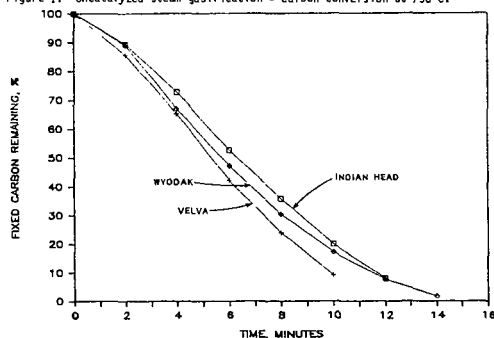
Figure 2. K_2CO_3 catalyzed steam gasification-carbon conversion at 750°C.
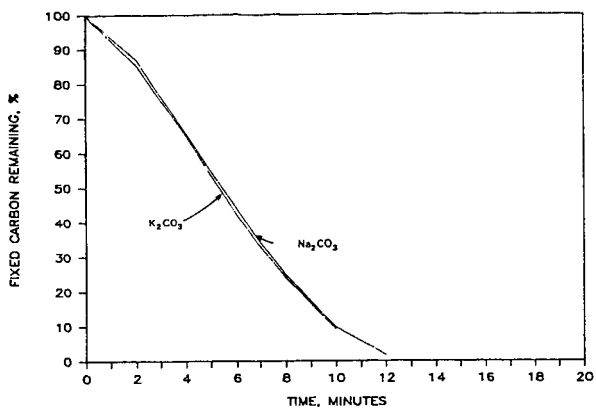
Figure 3. Catalysis of Velva lignite - steam gasification at 750°C.
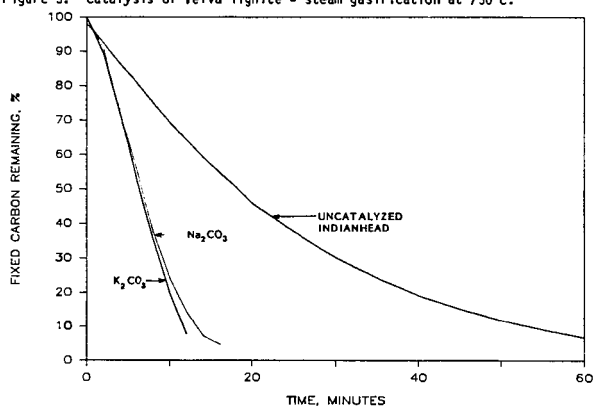
Figure 4. Catalysis of Indian Head lignite - steam gasification at 750°C.
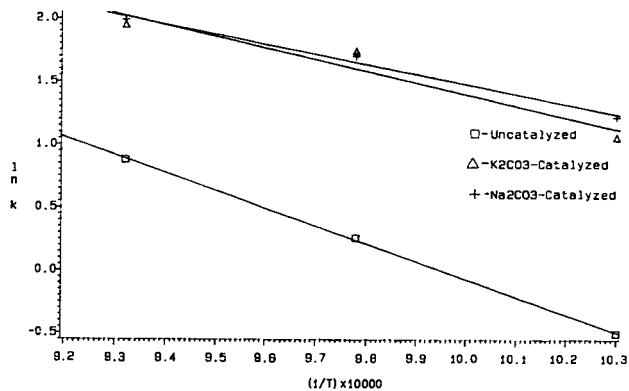

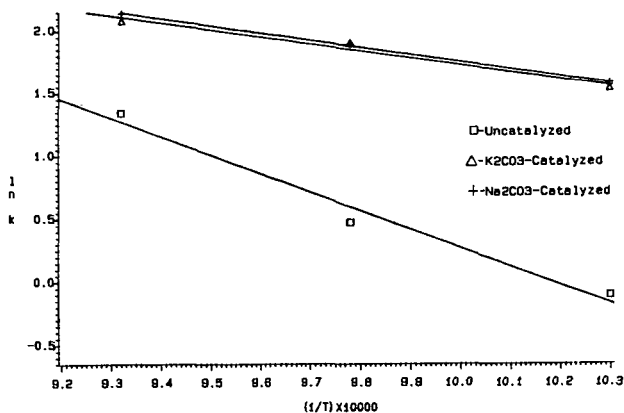Figure 5. Arrhenius plots of the reactivities of catalyzed and uncatalyzed Indian Head coal char with steam.

Figure 6. Arrhenius plots of the reactivities of catalyzed and uncatalyzed Velva coal char with steam.
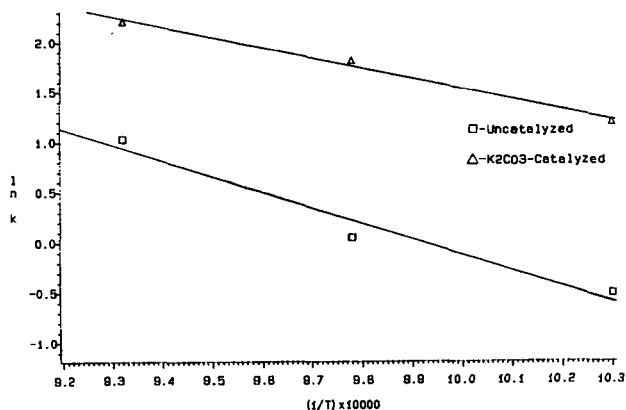

Figure 7. Arrhenius plots of the reactivities of catalyzed and uncatalyzed Wyodak coal char with steam.

Coal Swelling in n-Amines and n-Alcohols

Thomas K. Green and Thomas A. West

Department of Chemistry
Western Kentucky University
Bowling Green, KY   42101

Introduction. Recent studies of the solvent swelling of coals have yielded consider-
able insight into their macromolecular structure.(1-6) It is becoming increasingly
evident that hydrogen bond crosslinks play a central role in the swelling behavior
of many coals. Larsen and co-workers, for example, demonstrated that the degree of
swelling of two bituminous coals in good nonpolar solvents increases in the order
unextracted<pyridine-extracted <O-methylated and O-acetylated.(6) This order is
attributed primarily to the progressive disruption of the hydrogen bond crosslinks
in the coal. The unextracted coal contains many hydrogen bond crosslinks and since
the nonpolar solvent cannot disrupt them, the swelling remains low. The pyridine-
extraction serves to only partially disrupt the crosslinks. The crosslinks are
absent in the chemically-modified coals, and these coals can expand to contain the
solvent. Their ultimate dissolution is prevented by the presence of covalent
crosslinks.

The swelling of coals in polar solvents has also been studied extensively.(1-5,
7,8) Polar solvents are capable of interacting specifically with polar functional
groups in the coal. Amines are particularly effective, with the coal often doubling
in volume upon exposure to solvent. Brenner, for example, exposed a thin section
of Illinois No. 6 coal to vapors of n-propylamine.(1) The sample approximately
doubled in size, and the process was found to be highly reversible. The coal was
also found to be highly flexible in the swollen state. This flexibility is attributed
primarily to the breaking of coal-coal hydrogen bonds (i.e. crosslinks) by the n-pro-
pylamine during the swelling process.

Brenner's results suggest that the n-propylamine is hydrogen bonding to specific
sites within the Illinois No. 6 structure. If so, we thought the number of sites
might be quantified by solvent swelling measurements. We extended the study to in-
clude other n-alkylamines to see if they might behave similarly to n-propylamine.
The results on four different coals are presented and contrasted with those using
n-alkylalcohols as swelling solvents.

Experimental.
Swelling Measurements. All solvents were purified according to standard methods.(9)
The experimental technique has been previously described.(10) Briefly, about 100-
200 mg of dry coal was placed in a 7 mm o.d. Pyrex tube sealed on one end. The coal
was centrifuged at 1750 rpm for 5 minutes and the height of coal in the tube was
measured as h_1. Excess solvent (3-4 mL) was added to the tube, which was sealed with
a rubber stopper and immediately shaken. Periodically, the tube was shaken and
centrifuged again for 5 minutes. The height of swollen coal was measured as h_2.
The degree of swelling was calculated as Q, the swelling ratio.

$$Q = h_1/h_2 = \frac{\text{volume of swollen coal}}{\text{volume of unswollen coal}} \qquad 1)$$

The measurements were continued until no further change in Q occurred during a two
week period. All swelling measurements were conducted at ambient temperature.

Coal Analyses. The four coals used in the study were dried under vacuum at 110°C for
24 hrs prior to swelling. Their elemental analyses on a dry, mineral-matter-free
basis are presented in Table I.

TABLE I

Elemental Analyses of Coals (Wt %)

Coal	C	H	N	S_{org}	O^a	Mineral Matter
Wyoming Rawhide	72.3	5.2	0.95	0.51	21.0	7.5
Texas lignite	70.6	5.5	1.3	1.2	21.4	8.3
Illinois No. 6	78.9	5.6	1.4	3.4	10.7	14.0
Bruceton	85.4	5.7	1.5	0.7	6.7	6.1

[a] by difference

Results.
Swelling in n-Alkylamines. A series of n-alkylamines were used as swelling solvents for the various coals. The swelling ratios are presented in Table II. Each value represents the average of 3 or 4 measurements and the reproducibility was on the order of ±3 percent. The pyridine-extracted (Soxhlet) Illinois No. 6 and Rawhide coals were also studied to determine what effect the extraction process might have on the equilibrium swelling ratios. The extractabilities were found to be 18.3 percent and 5.8 percent for the Illinois No. 6 and Rawhide coals, respectively.

The calculated amounts (mmoles) of solvent absorbed per g of dmmf coal are also presented in Table II. The values were calculated according to the equation

$$\frac{\text{mmoles absorbed}}{\text{g of dmmf coal}} = \frac{(Q - 1)}{\rho \ V} \times 1000 \qquad \qquad 2)$$

where Q is the swelling ratio, V is the molar volume of the solvent at $25°C$, and ρ is the density of the coal. A value of 1.3 g/mL was assumed for the density of all coals. This calculation assumes additivity of volumes between coal and solvent. This assumption was not tested.

TABLE II

Swelling Data of n-Alkylamines and Four Coals

	Bruceton Unextracted		Illinois No. 6 Unextracted		Extracted	
Solvent	Q	mmoles abs g dmmf coal	Q	mmoles abs g dmmf coal	Q	mmoles abs g dmmf coal
n-propylamine	1.80	7.5	2.04	9.7	2.21	11.3
n-butylamine	2.09	8.5	2.23	9.6	2.25	9.8
n-hexylamine	2.32	7.7	2.72	10.0	2.62	9.4
n-octylamine	2.61	7.5	2.94	9.0	2.79	8.3
Average:		7.8		9.6		9.7

	Big Brown Unextracted		Rawhide Unextracted		Extracted	
	Q	mmoles abs g dmmf coal	Q	mmoles abs g dmmf coal	Q	mmoles abs g dmmf coal
n-propylamine	2.64	15.3	2.30	12.2	2.22	11.4
n-butylamine	2.94	15.1	2.44	11.2	2.34	10.4
n-hexylamine	3.27^a	13.2^b	3.03	11.8	2.74	10.1
n-octylamine	3.14^a	10.0^b	3.14^a	10.0^b	3.08^a	9.7^b
Average:		15.2		11.2		10.6

[a] Not at equilibrium after 1200 hrs.
[b] Excluded from average because swelling had not reached equilibrium.

Swelling in n-Alkyl Alcohols. A series of n-alkyl alcohols were used to swell the
Bruceton and Big Brown coals so that the results could be compared with those using
the n-alkylamines as swelling solvents. The swelling ratios and the amounts absorbed
by the coals are presented in Table III.

TABLE III

Swelling Data for n-Alkyl Alcohols and Two Coals

| | Bruceton Unextracted | | Big Brown Unextracted | |
Solvent	Q	mmoles abs g dmmf coal	Q	mmoles abs g dmmf coal
methanol	1.18	3.4	1.67	12.7
n-propanol	1.20	2.6	1.69	9.0
n-butanol	1.21	2.2	1.66	6.8
n-hexanol	1.20	1.2	1.33	2.0
n-octanol	1.22	1.1	1.30	1.5

Discussion.
Swelling in n-Alkylamines. The degree of swelling of each coal is observed to increase
linearly with increasing size of the amine. This result is shown in Figure 1, where
Q is plotted against the molar volume of the solvent. Bruceton coal swells the least
in each solvent, whereas Big Brown lignite swells the most. (Note that some Q values
were omitted from Figure 1 since they were not equilibrium values).
     As shown in Table II, each coal absorbs nearly a constant amount of each amine.
This result suggest that the amines are binding to specific sites within the coal,
and that each amine, regardless of its size, has equal accesibility to the binding
sites. The degree of swelling increases with increasing chain length of the amine
because the coal network must expand more to accommodate the larger alkyl groups.
     The amines are probably interacting through hydrogen bonding with oxygen func-
tionalities in the coals, since oxygen is the most abundant heteroatom in the coals
and the amines are known to be strong hydrogen bonding solvents. If this is true,
then the amounts of amine absorbed by the coals should roughly correlate with the
oxygen contents of the coals. This general trend is observed, with the amounts of
amine absorbed by the coal increasing in the order Bruceton < Illinois No. 6 < Rawhide
< Big Brown lignite. The amines are probably hydrogen bonding to phenolic hydroxyl
groups in the coal. However, the amounts absorbed by the coals exceed the number
of phenolic hydroxyl groups known to be present in the coals. For example, Illinois
No. 6 and Rawhide coals are reported to contain approximately 3 and 5 mmoles hydroxyl
groups per g of dmmf coal.(11,12) These amounts are much less than the amounts of amine
absorbed by the coals (see Table II). Apparently, the amines are interacting with
other sites in the coals as well. These sites may include ether and carboxylic
functional groups, which are known to be present in coals.
     Although a detailed kinetic study was not undertaken, approximate times to
equilibrium swelling were measured for some coals and solvents. Equilibrium times
varied dramatically, depending upon both coal and solvent. These results are pre-
sented in Table IV for three coals and n-butyl- and n-octylamine. The coals reached
equilibrium much faster in n-butylamine than in n-octylamine. The bulky octyl group
apparently prevents rapid diffusion of the amine into the coal network. The equi-
librium times in n-octylamine increase in the order Illinois No. 6 < Rawhide < Big
Brown. The n-octylamine–Big Brown system was still not at equilibrium after 1200
hrs, demonstrating that coal swelling can be an extraordinarily slow process.

TABLE IV

Approximate Swelling Times for
n-Butylamine and n-Octylamine and Three Coals

Solvent	Illinois No. 6	Rawhide	Big Brown
n-butylamine	1 hr	1 hr	5 hrs
n-octylamine	5 hrs	170 hrs	1200 hrs[a]

[a] Not at equilibrium after 1200 hrs.

Finally, pyridine-extracted Illinois No. 6 and Rawhide coals were also studied to determine what effect the extraction process has on the equilibrium swelling ratios. The results in Table II reveal that the extracted coals swell to nearly the same degree as the unextracted coals, with nearly the same average amounts of amine being absorbed. The results suggest that the amines are interacting with the unextracted and extracted coals in a similar fashion, and that the binding sites within the coals are equally accessible to the amines.

Swelling in n-Alkyl Alcohols. Bruceton coal and Big Brown lignite were swollen in a series of n-alkyl alcohols in order determine if they behaved similarly to the amines. As shown in Figure 1, the swelling ratios remain constant at about 1.2 for the Bruceton coal, regardless of the size of the alcohol. For Big Brown lignite, three of the smaller alcohols give swelling ratios of 1.65. The swelling drops off for n-hexyl alcohol and n-octyl alcohol, suggesting that these swelling ratios are not yet at equilibrium. As with the amines, the alcohols swell the lignite more than the Bruceton coal.

The amounts of alcohol absorbed are seen to decrease with increasing size of the alcohol as shown in Table III. Thus the alcohols do not have equal accessibility into coal network, in contrast to the amines. These results are consistant with calorimetry studies of Wightman and Widyani, who measured the heats of immersion of a Pocahontas No. 3 coal in series of n-alkyl alcohols.[13] They observed the heats of immersion to decrease with increasing size of the alcohol, and concluded that the smaller alcohols were able to penetrate the coal structure more easily than the larger alcohols.

The different behaviors of the amines and the alcohols toward the coals must be related to the strengths of the coal-solvent interactions. The amines interact much more strongly with the coals than the alcohols because the degree of swelling is much greater in the amines. The amines can be expected to disrupt coal-coal hydrogen bond crosslinks and, by doing so, the coal will be much more flexible. The coal is then able to expand to contain even the large n-octylamine. The alcohols apparently lack this ability to disrupt the hydrogen bond crosslinks since the amounts absorbed by the coals decrease with increasing size of the alcohol instead of remaining constant.

Conclusion. The swelling of four different coals in series of n-alkylamines and n-alkyl alcohols were measured. For the amines, the amounts absorbed by the coals remains constant among the series, suggesting that the amines are binding to specific sites within the coal network. Thus, the principal driving force for the swelling process is enthalpic in nature for these solvents. The alcohols behave quite differently toward the coals, with the amounts absorbed by the coal decreasing with increasing size of the alcohol. This difference in behavior is attributed primarily to the inablity of the alcohol to disrupt the hydrogen bond crosslinks of the coal network.

The swelling ratios of the coals in other larger n-alkylamines can be predicted from the results presented in Figure 1. For example, Big Brown lignite and Bruceton coal are predicted to have Q values of 7.8 and 3.5, respectively, in octadecylamine. However, the swelling process will probably be extraordinarily slow in this solvent, possibly requiring several months o_r years to reach equilibrium at room temperature.

The covalently crosslinked nature of the coal may also place a limitation on how much it will swell in larger n-alkylamines. For example, the lignite must expand to nearly 8 times its original volume in order to accommodate the predicted amount of octadecylamine. The existence of covalent crosslinks may prevent this degree of expansion. The swelling ratio may, in fact, level off at some critical amine size. Several factors will probably play a role in determining this critical size, including the strength of the coal-solvent interaction, the population of the oxygen functionalities in the coal, the covalent crosslink density of the coal, and the flexibility of the macromolecular chains.

References

(1) D. Brenner, Fuel 1984, 63, 1325.
(2) D. Brenner, Fuel 1985, 64, 167.
(3) N. A. Peppas, L. M. Lucht, M. E. Hill-Lievense, and D. T. Hooker, "Macromolecular Changes in Bituminous Coal During Extraction and Solubilization," Final Technical Report, Contract No. DE-F22-80PC30222, PETC, Department of Energy, 1983.
(4) H. P. Hombach, Fuel 1980, 59, 465.
(5) J. R. Nelson, O. P. Mahajan, and P. L. Walker, Jr., Fuel 1980, 59, 831.
(6) T. K. Green, J. W. Larsen, and I. C. Chiri, Proc. Int. Conf. Coal Sci. 1983, 277.
(7) N. Y. Kirov, J. M. O'Shea, and C. D. Sergeant, Fuel 1967, 43, 615.
(8) Y. Sanada and H. Honda, Fuel 1967, 46, 451.
(9) D. D. Perrin, W. L. F. Armarego, and P. R. Perrin, "Purification of Laboratory Chemicals," 2nd Ed., Pergamon Press, 1980.
(10) T. K. Green, J. Kovac, J. W. Larsen, Fuel 1985, 63, 935.
(11) R. Liotta, K. Rose, and E. Hippo, J. Org. Chem. 1981, 46, 277.
(12) R. Liotta, G. Brons, J. Am. Chem. Soc., 1981, 103, 1735.
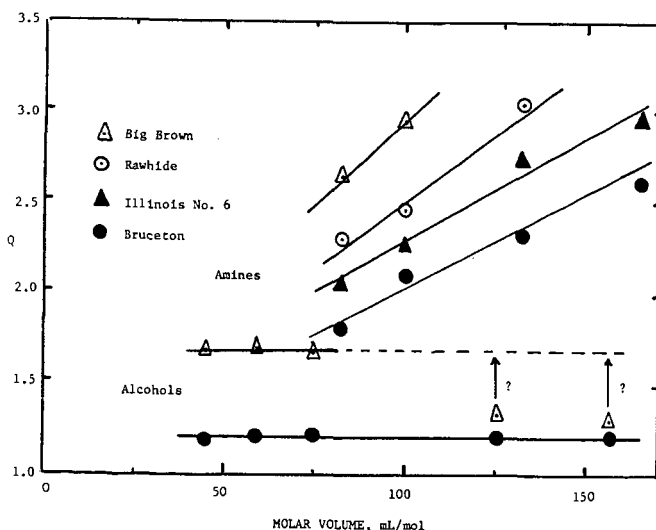(13) E. Widyani and J. P. Wightman, Coll. Surf. 1982, 4, 209.

FIGURE 1. Plot of Swelling Ratios against Molar Volume of Solvent for a Series of n-Alcohols and n-Amines and Several Coals.

THE RUTHENIUM(VIII) CATALYZED OXIDATION OF TEXAS LIGNITE AND ILLINOIS NO. 6 BITUMINOUS COAL. THE ALIPHATIC AND AROMATIC CARBOXYLIC ACIDS.
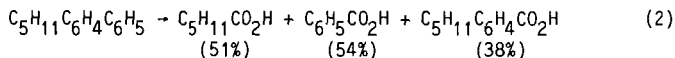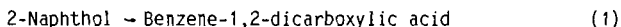
Leon M. Stock, Kwok-Tuen Tse and Shih-Hsien Wang

Department of Chemistry, University of Chicago, Chicago, IL 60637

INTRODUCTION

The structural elements in coals have been under study by modern methods in several laboratories over the past decade. Deno and his associates pointed out the need for specific reagents for the elaboration of the aliphatic network in these materials and have exploited the acid-catalyzed reactions of peroxyacids for the selective decomposition of the aromatic structural elements (1-5). Unfortunately, the initial reaction products are often unstable under the reaction conditions and it is difficult to relate the structures of the observed products to the original structural elements of the coals (5). Considerations of this kind and other objectives led us to consider the use of ruthenium(VIII) as an oxidant for coal. Sharpless and his associates recently pointed out that oxidation reactions with ruthenium(VIII) could be carried out very effectively in the presence of acetonitrile (6). Their suggestion led to the discovery that ruthenium(VIII) in a nitrile-rich solvent was an excellent oxidant for coal (7).

The oxidation reactions of representative hydrocarbons such as the alkylbenzenes, alkylnaphthalenes, phenanthrenes and anthracenes have been investigated (7). The selectivity of the reaction is illustrated by the results for the oxidation of 2-naphthol and 4-pentylbiphenyl, equations (1) and (2).

$$2\text{-Naphthol} \rightarrow \text{Benzene-1,2-dicarboxylic acid} \qquad (1)$$

$$C_5H_{11}C_6H_4C_6H_5 \rightarrow C_5H_{11}CO_2H + C_6H_5CO_2H + C_5H_{11}C_6H_4CO_2H \qquad (2)$$
$$\phantom{C_5H_{11}C_6H_4C_6H_5 \rightarrow} (51\%) \qquad\quad (54\%) \qquad\quad (38\%)$$

The reagent has also been used successfully for the oxidation of Illinois No. 6 coal (7). Further, the volatile monocarboxylic acids have been determined quantitatively using the oxidation reaction in conjunction with isotope dilution techniques (10). Mallya and Zingaro investigated the oxidation of Texas lignite using ruthenium(VIII); they pointed out that ester groups were produced during the reaction (8). Olson and his coworkers employed the reagent and a phase transfer catalyst for the oxidation of North Dakota lignite; they identified 16 principal products (9).

This report concerns the similarities and differences we observed in the product distribution obtained in the oxidation of Texas lignite and Illinois No. 6 coal.

493

EXPERIMENTAL PART

Materials.--Ruthenium(III) chloride trihydrate, carbon tetrachloride, acetonitrile, and ether were obtained from commercial sources. Authentic samples of the carboxylic acids or esters were obtained from commercial sources and from R. Hayatsu and R.E. Winans of the Argonne National Laboratory. Diazomethane was prepared from Diazald.[R]

Illinois No. 6 coal [77.2%C, 5.6%H, 0.68%N, 0.15%Cl, 2.95% organic S, 0.89% pyritic S, 0.00% sulfate, and 12.5% O (by difference)] was obtained from the Peabody mine in Pawnee, Illinois. Texas lignite [70.0% C, 5.0% H, 1.5% N, 2.0% S, 19.6% O (by difference)] was obtained from the Wilcox formation near Rockdale, Texas and was supplied by N. Mallya. Each sample was extracted before oxidation with aqueous hydrochloric acid, aqueous sodium hydroxide, benzene-methanol, and chloroform as described by Hayatsu and coworkers (11).

Oxidation Procedure.--The oxidation reactions were carried out as described previously (7) using coal (400 mg), ruthenium(III) chloride trihydrate (12 mg), and sodium periodate (4 g) in a mixture of carbon tetrachloride (8 ml), acetonitrile (8 ml) and water (12 ml). The mixture was stirred for about 24 hours at room temperature. The solids were collected by filtration and the organic and the aqueous phases were retained. The mildly acidic aqueous layer was washed with four portions of ether (15 ml). The solid was also washed with ether. All the organic extracts were combined and dried with sodium sulfate. The solvents were removed with a rotary evaporator at 40°C. The acids in the concentrated solution were methylated using 0.35M diazomethane in ether (10 ml). The ether was carefully removed using a rotary evaporator at room temperature. This procedure was repeated three times and the final solution was examined by gas chromatography/mass spectrometry.

Gas Chromatography Mass Spectrometry.--The GC/MS results were obtained using an HP Model 5790A gas chromatograph with VG Model 70-250 mass spectrometer. The chromatograph was equipped with a 50 meter, OV-1701 (0.25µ) capillary column supplied by Quadrex Corporation for the analysis of the oxidation products of the Illinois No. 6 coal. The conditions for the analysis are noted: injection port, 250°C; the oven temperature was programmed to hold at 50°C for one minute then to heat to 270°C at the rate of 7°C/min and then to hold at 270°C. The entire oxidation procedure and analysis was repeated. The gas chromatograms of the products are shown in Figures 1a and 1b.

In the analysis of Texas lignite, a 60 meter Durabond 1701 (0.25µ) capillary column supplied by J & W Scientific Inc. was used. The conditions for the analysis are noted: injection port, 250°C, the oven temperature was programed to hold at 50°C for one minute, and to heat to 270°C at the rate of 8°C/min and then to hold at 270°C. The gas chromatogram of the oxidation product of Texas lignite is shown in Figure 2.

One scan per second was used in low resolution electron impact (EI) and chemical ionization (CI) mass spectral analyses. Isobutane was used as the reagent gas in the chemical ionization work.

RESULTS

The oxidation reactions of Texas lignite and Illinois No. 6 bituminous

coal proceeded smoothly with the ruthenium ion catalyst and the carboxylic acids were isolated without difficulty. The esterification reactions were carried out exhaustively to insure that substances such as benzenetetracarboxylic acid were completely converted to the corresponding methyl esters. Capillary gas chromatography as described in the Experimental Part provided an excellent separation of the esters. In many cases, the structures of the products were established by comparison with authentic samples. When authentic samples were not available, electron impact and chemical ionization mass spectrometry were used to assign their structures in conjunction with libraries of mass spectral data. These procedures enabled the identification of about 100 compounds including virtually every compound formed in greater than 5% yield relative to dimethyl butane-1,4-dioate. It is notable that neither nitrogen- nor sulfur-containing compounds have been detected among the reaction products of these coals. Accordingly, we are continuing our study of the less abundant substances and of the substances that are not fully resolved by capillary chromatography.

The results for the more prominant benzene and aliphatic carboxylic acids are summarized in Tables 1 and 2.

DISCUSSION

Benzenecarboxylic Acids.--Ruthenium(VIII) is a selective electrophilic oxidant. Phenolic compounds and activated polycyclic aromatic compounds are oxidized to benzenecarboxylic acids by the reagent (7). Neither phenolic compounds nor ethers, for example 4-hydroxy- or 4-methoxybenzenecarboxylic acid, nor reactive aromatic compounds, for example naphthalene-2-carboxylic acid, are observed among the oxidation products. Rather, the reaction provides a broad array of benzenecarboxylic acids, some of which have methyl, methylene- carboxyl (CH_2CO_2H) or oxocarboxyl ($COCO_2H$) groups bonded to the benzene ring. The absence of hydroxyl and methoxyl derivatives in the products coupled with a knowledge of the carbon atom balance strongly suggests that the benzenecarboxylic acids observed in this reaction account virtually quantitatively for the oxygen-free carbocyclic structures in these coals.

Five important features are apparent in the results for Texas lignite. Only 10-15 mole % of the products are benzenecarboxylic acids. Among these acids, benzene-1,2-dicarboxylic acid is the most abundant product. Neither benzene-1,3-, benzene-1,4-dicarboxylic acid, nor benzene-1,3,5-tricarboxylic acid are formed in the reaction. Benzene-1,2-dicarboxylic acid, benzene- 1,2,3-, benzene-1,2,4-tricarboxylic acid, and benzene-1,2,4,5-tetracarboxylic acid are produced in a 20:20:10:1 ratio. A variety of methylbenzenecarboxylic acids are also obtained.

These results provide cogent evidence for the view that ortho substitution patterns are predominant in the carbocyclic structures of this material and that biphenyl structures are insignificant. The more abundant benzenedi- and tricarboxylic acids presumably arise from naphthalenes, naphthols, and oxygen- containing heterocyclic compounds. The low abundances of the tetracarboxylic acids indicate that the carbocyclic structures are not condensed to a significant degree. Thus, the results are incompatible with an important role for phenanthrenes or anthracenes.

---

*For convenience, the products are described as carboxylic acids rather than methyl esters in this discussion.

The Illinois No. 6 coal undergoes ruthenium(VIII) oxidation to yield a very different array of benzenecarboxylic acids. In this instance, benzene-carboxylic acids constitute about 25-30 mole % of the product. Benzene-1,2-dicarboxylic acid, benzene-1,2,3- and 1,2,4-tricarboxylic acids and benzene-1,2,4,5-tetracarboxylic acid are the most prominant products. Only very small quantities of benzene-1,3- and 1,4-dicarboxylic acid and benzene-1,3,5-tri-carboxylic acid are formed. Benzene-1,2-dicarboxylic acid, benzene-1,2,3-, benzene-1,2,4-tricarboxylic acid, and benzene-1,2,4,5-tetracarboxylic acid are formed in a 0.8:0.9:1.2:1 ratio. This oxidation product also contains a variety of methylbenzenecarboxylic acids.

The product distribution for Illinois No. 6 coal contrasts sharply with that for Texas lignite. The most prominant differences appear in the large increase in the yields of the tri- and tetracarboxylic acids which indicate that the carbocyclic network of the Illinois coal is significantly more con-densed than that of the lignite.

The oxidation reactions of these coals also yield aliphatic monocarboxy-lic acids (10). Acetic acid is the predominant product of this kind. Quanti-tative analyses indicate that the Illinois No. 6 coal used in this study yields 1.7 moles of acetic acid/100 carbon atoms. This acid arises principally from the oxidation of methylated aromatic fragments. The results presented in Table 1 indicate that avariety of other methylated compounds are also formed. Seve-ral lines of evidence now suggest that Illinois No. 6 coals contain between 4 and 6 methyl groups per 100 carbon atoms (10,12).
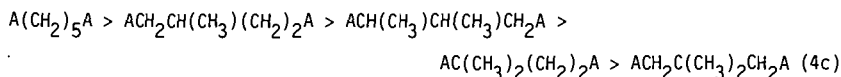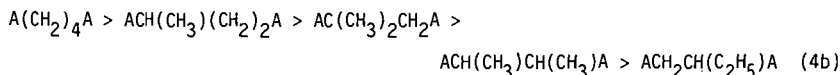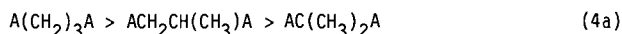
Aliphatic Carboxylic Acids.--Ruthenium(VIII) reacts selectively with acti-vated aromatic structures. Most aliphatic structures are stable. Thus, alkyl-aromatic compounds provide the corresponding alkylcarboxylic acids ($RAr \rightarrow RCO_2H$), hydroaromatic compounds provide dicarboxylic acids (indan $\rightarrow$ pentane-1,5-dioic acid) and bridging alkyl fragments yield dibasic acids (bibenzyl $\rightarrow$ butane-1,4-dioic acid). Most aliphatic acids are stable under the reaction conditions. Unfortunately, the propane-1,3-dioic acids decompose as illustrated for the ethyl derivative in equation (3).

$$CH_3CH_2CH(CO_2H)_2 \rightarrow CH_3CH_2CO_2H \qquad (3)$$
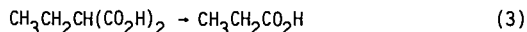
In spite of this limitation, the ruthenium(VIII) oxidation provides both a better yield of aliphatic acids and a more diverse array of products than other oxidants such as the peracids (2,3).

The aliphatic reaction products obtained from Texas lignite and Illinois No. 6 coal are summarized in Table 2.

The oxidation of Texas lignite provides about 60 aliphatic acids. Vir-tually all of the acids produced in greater than 5% abundance relative to butane-1,4-dioic acid have been identified. All the α,ω-diacids from butane-1,4-dioic acid to undecane-1,11-dioic acid are present. Many other diacids are also produced including almost every isomer of the 5,6, and 7 carbon atom derivatives as illustrated in equation (4). An interesting array of tri- and tetracarboxylic acids are also formed.

$$A(CH_2)_3A > ACH_2CH(CH_3)A > AC(CH_3)_2A \qquad\qquad (4a)$$

$$A(CH_2)_4A > ACH(CH_3)(CH_2)_2A > AC(CH_3)_2CH_2A >$$
$$ACH(CH_3)CH(CH_3)A > ACH_2CH(C_2H_5)A \quad (4b)$$

$$A(CH_2)_5A > ACH_2CH(CH_3)(CH_2)_2A > ACH(CH_3)CH(CH_3)CH_2A >$$
$$AC(CH_3)_2(CH_2)_2A > ACH_2C(CH_3)_2CH_2A \quad (4c)$$

The interpretation of these results is complicated by the fact that several of the products can be formed in different ways. To illustrate, pentane-1,5-dioic acid can be formed from four different structures: $Ar(CH_2)_3Ar$, $Ar-(CH_2)_3CH(Ar)_2$, indan, and 1-aryltetralin. Nevertheless, the results provide a basis for the discussion of the complex aliphatic network in this coal.

The product mixture obtained from Illinois No. 6 coal is much less complex. About 40 compounds have been identified. In contrast to the lignite, only 5 α,ω-dicarboxylic acids are obtained and there are correspondingly fewer di- and tricarboxylic acids. There is a considerable decrease in the quantities of the higher molecular weight aliphatic acids.

The product distribution observed in this study is considerably more diverse than that obtained in previous studies of the aliphatic network of this coal. Many of the aliphatic acids produced in the reaction of the lignite are also formed from this coal during oxidation, but the yields are uniformly lower. Thus, the structures of the two materials appear to be closely related.

CONCLUSION

Ruthenium(VIII) is a selective oxidant for activated aromatic compounds and, therefore, provides definite information concerning the less readily oxidized carbocyclic and aliphatic structural elements in these coals. There are significant differences in the benzenecarboxylic acid product distributions for Texas lignite and Illinois No. 6 bituminous coal. While it is clear that ortho structures are dominant in the two coals, the degree of condensation differs appreciably for these 70 and 77%C (daf) materials. Hayatsu and co-workers have commented on this difference previously (13). Ruthenium(VIII) oxidation provides the aliphatic mono-, di-, tri- and tetracarboxylic acids in greater quantity and structural diversity than other techniques, such as per-acid oxidation (2,3), designed to elaborate this structural element. Both Texas lignite and Illinois No. 6coal yield many of the same low molecular weight di- and tri- carboxylic acid. While it is evident that the aliphatic structure of the lignite is more diverse, the structures of the two coals appear to be correlated inasmuch as many of the products have similar three and four carbon fragments. Broadly, our results are compatible with the view-point that the carbocyclic aromatic network becomes more diverse and the aliphatic network less diverse as coalification proceeds.

REFERENCES

1) N.C. Deno, B.A. Greigger and S.G. Stroud, Fuel, 57, 455 (1978)

2) N.C. Deno, K.W. Curry, B.A. Greigger, A.D. Jones, W.G. Rakitsky, K.A. Smith, K. Wagner and R.D. Minard, Fuel, 59, 694 (1980)

3) N.C. Deno, K.W. Curry, A.D. Jones, K.R. Keegan, W.G. Rakitsky, C.A. Richter and R.D. Minard, Fuel, 60, 210 (1981)

4) R.K. Hessley, B.M. Benjamin and J.W. Larsen, Fuel, 61, 1085 (1982)

5) D. Dumay, G. Kirsch, R. Gruber and D. Cagniant, Fuel, 63, 1544 (1984)

6) P.H.J. Carlsen, T. Katsuki, V.S. Martin and K.B.J. Sharpless, J. Org. Chem., 46, 3936 (1981)

7) L.M. Stock and K.T. Tse, Fuel, 62, 974 (1983)

8) N. Mallya and R.A. Zingaro, Fuel, 63, 423 (1984)

9) E.S. Olson and J.W. Diehl, ACS, Division of Fuel Chem. Preprints, 29(6), 217 (1984)

10) L.M. Stock and S.H. Wang, Fuel, accepted for publication (1985)

11) R. Hayatsu, R.E. Winans, R.G. Scott and R.L. McBeth, Fuel, 60, 158 (1981)

12) P. Painter, M. Starsinic, E. Riessen, C. Rhoads and B. Bartges, ACS, Division of Fuel Chem. Preprints, 29(1), 29 (1984)

13) R. Hayatsu, R.G. Scott, R.E. Winans, "Oxidation in Organic Chemistry", Part D, Chapter IV, Academic Press, Inc., New York (1982).

Table 1. The Benzenecarboxylic Acids Formed in the Oxidation of Texas Lignite and Illinois No. 6 Coal.

Compound	Texas Lignite Number	Abundance[a]	Illinois No. 6 Number	Abundance[a]
Benzenemonoacid		W		W
Benzene-1,2-diacid		VS		S
Benzene-1,3-diacid	Not detected			VW
Benzene-1,4-diacid	Not detected		Not detected	
Methylbenzenediacids[b]	4	2M,2W	2	W,M
Dimethylbenzenediacids[b]	1	VW	1	VW
Benzene-1,2,3-triacid		S		VS
Benzene-1,2,4-triacid		VS		VS
Benzene-1,3,5-triacid		VW		VW
Methylbenzenetriacids[b]	5	VW	5	4W,1VW
Dimethylbenzenetriacids[b]	2	VW	2	VW
Trimethylbenzenetriacids[b]	Not detected		4	3W,1M
Benzene-1,2,3,4-tetraacid		W		M
Benzene-1,2,3,5-tetraacid		W		VW
Benzene-1,2,4,5-tetraacids		W		VS
Methylbenzenetetraacids[b]	1	VW	2	1M,1VW
Dimethylbenzenetetraacids[b]	Not detected		1	W
Benzenepentaacid	Not detected			VW

[a]The relative abundances are based upon the relative ion currents with dimethyl butane-1,4-dioate adopted as 100%. The notation is VS > 30%; S 15-30%; M 5-15%; W 2-5% and VW < 2%.

[b]Certain of the methyl-containing molecules have CH_2CO_2H fragments rather than simple methyl groups.

Table 2. The Relatively Abundant Aliphatic Carboxylic Acids Formed in the Oxidation of Texas Lignite and Illinois No. 6 Coal.

Compound[a]	Texas Lignite		Illinois No. 6	
	Number	Abundance[a]	Number	Abundance[a]
2C2A	1	VS	1	VS
3C2A	3	2VS,1W	3	2VS,1W
4C2A	5	2VS,1M,1W,1VW	3	2S,1VW
5C2A	7	1VS,4M,2W	6	2M,2W,2VW
6C2A	7	1VS,3W,3VW	2	1W,1VW
7C2A	4	1VS,1S,1W,1VW	-	-
8C2A	1	VW	-	-
9C2A	1	M	-	-
10C2A	2	1M,1VW	-	-
11C2A	1	W	-	-
3C3A	1	VS	1	S
4C3A	5	1S,4M	5	1M,3W,1VW
5C3A	5	4M,1W	4	4W
6C3A	6	2M,4VW	1	W
7C3A	3	1M,2VW	-	-
4C4A	1	VW	-	-

[a]The numbers of unoxidized aliphatic carbon atoms in the structure are indicated first, followed by the number of acid groups. Thus, 2C2A could be 1,4-butanedioic acid or 2-methyl-1,3-propanedioic acid.

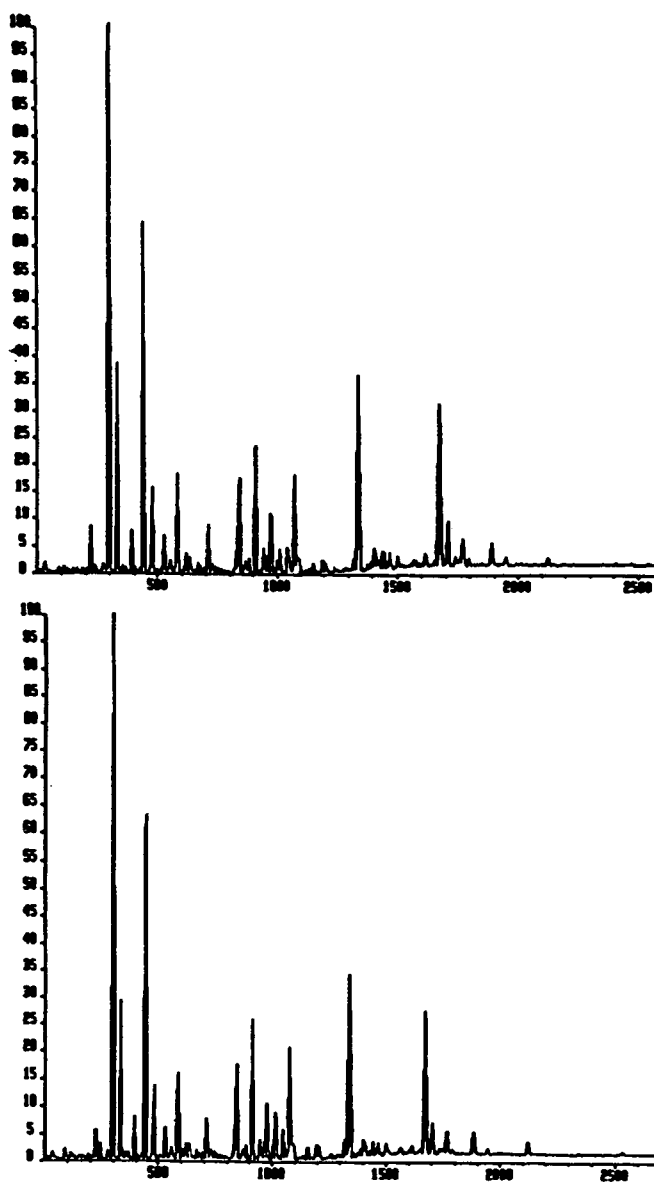[b]The abundance is defined in footnote b of Table 1.

Figure 1. Chromatograms (GCMS) of the oxidaiton products of Illinois No. 6 coal obtained in fully independent experiments.
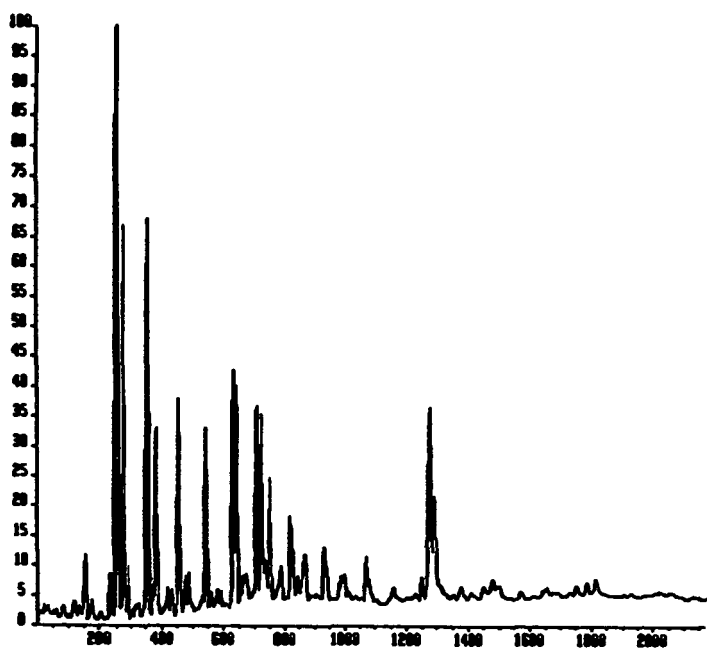
Figure 2. Chromatogram (GCMS) of the oxidation product of Texas lignite.